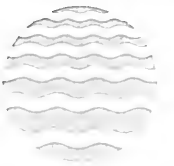
STOPPING WATER POLLUTION AT ITS SOURCE



MISA

Municipal-Industrial Strategy for Abatement

DRAFT PROTOCOL FOR THE SAMPLING AND ANALYSIS OF INDUSTRIAL/MUNICIPAL WASTEWATER

Ontario

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DRAFT PROTOCOL FOR THE SAMPLING AND ANALYSIS OF INDUSTRIAL/MUNICIPAL WASTEWATER

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Table of Contents

ATG M1 to ATG M13 are sector specific parameters which were required to be analyzed under the monitoring regulations. For example: IC1, chloride, was required under the Inorganic Chemical Sector Regulation and has now been listed under ATG M1. Under the Pulp and Paper Sector Regulation, dehydroabietic acid was listed separately: in this protocol the compound is listed only under ATG 26, resin and fatty acids.

1.0 INTRODUCTION

This section will provide the user with an overall view of the intent, scope and limitations of this guidance document. Additionally, the user is provided an insight as to the format and content of the main body of the document (Section 5, Guidelines for Individual MISA Analytical Test Groups - ATG) which will serve as a key on 'How To Use This Manual'.

1.1 **Purpose**

The MISA program was initiated with a series of sector specific monitoring regulations which referred to a common General Regulation (Effluent Monitoring Regulation, General: Ontario Regulation 695/88 as amended to Ontario Regulation 533/89). The General Regulation contained, among other things: the common requirements, guidelines, principles and protocols related to the sampling, preservation, storage and analysis of wastewater samples; the minimum numbers and types of field and laboratory quality control samples to be included and a general guideline for data reporting.

The purpose of this guidance document is to capture those elements related to sampling, analysis and quality control; update, refresh and modernize the contents and, finally, present the information in a more convenient, user-friendly, style.

In this manner, the requirements, guidelines, principles and protocols retain their original force as dictated by regulations but they are also transformed into a more understandable, plain-english handbook.

1.2 **Scope**

This Guidance Document contains much of the same information originally presented in the General Regulation. It includes direction on techniques for: sampling of industrial/municipal wastewater; preserving of samples and their storage requirements; maximum storage times allowed prior to analysis; the most appropriate, and where applicable, alternate preparation and instrumental analysis protocols; and the type and frequencies of field and laboratory QC samples. This document represents a synthesis of best available information from organizations including Ontario Ministry of Environment, Environment Canada, Standard Methods, US Environmental Protection Agency (Federal

Register CFR40 part 136). It also incorporates the recommendations and conclusions reached through collaborative efforts of government, industrial and private laboratory personnel.

1.3 **Limitations**

This Guidance document defines the principles and protocols within which all laboratories must handle MISA samples. It intentionally stops short of stipulating any detailed procedures, methods or control techniques. While this approach can leave room for interpretation and uncertainty resulting in slight differences of sampling or analytical application, it also leaves room for improvement, analyst discretion and modernization of techniques which can improve the quality of environmental analytical data being generated.

The staff of the Ministry laboratories have tried to provide as much guidance as possible and to effectively link associated information. Any remaining shortcomings of this document will be addressed by knowledgeable laboratory staff from the government and private sector.

1.4 **Updates/Revisions**

This guidance document will be reviewed on a regular basis. Changes will be incorporated which represent an improvement, refinement or advancement in environmental science based on best scientific judgement, and/or peer review.

One specific area of update and revision - analytical methods - will be handled through a formal process described in the document Procedure and Criteria for Evaluating New Instrumental Measurement Method Principles for the Municipal and Industrial Strategy for Abatement (MISA) Program (NIMMP - October 1989) whereby a joint government/industry/laboratory panel will assess industry/laboratory recommendations for changes.

1.5 **Format and Content**

The heart of this guidance document is Section 5 - Guidelines for Individual MISA Analytical Test Groups (ATG) which is presented as a series of tables which contain all the information related to sampling, analysis and QC for each MISA ATG. The information is presented in a consistent format for ease of reference.

The information is presented in the form of guiding principles and protocols related to each component of sampling, analysis and quality control. While there are no specific methods identified,

there are recommended and alternate techniques clearly listed. Every effort should be made to apply the recommended techniques with adherence to good laboratory and sound quality control practices. There is sufficient latitude in the principles and protocols provided to allow for the customization of any specific sampling and analysis method to best suit the wastewater being assessed. All applied methods of sampling and analysis must however embody the principles and protocols listed.

In some rare cases, there may be an entry indicating that a sampling or analysis approach is not recommended. This is based on best available information of sampling and analysis techniques that suggest the techniques are either too complex, not cost effective or not sufficiently sensitive or rugged to provide useful samples or analytical data. This does not absolutely exclude the use of the identified technique but serves more as a precaution or warning.

The format and content of these tables provide all the information on a given ATG in an easy to read, comprehensive, fashion. For the sake of quick reference, the information is also presented in a checklist style in the appended schedules.

The following provides an outline of the topics addressed:

SAMPLING

This block outlines all requirements related to: sampling techniques; containers; container pretreatment; preservation; storage; sample volume recommendations and any associated notes, precautions or remarks. The information is presented with recommended, alternate and, in some cases, not recommended approaches.
This block is also presented as a short checklist or user's aid in Schedule 2.

ANALYSIS

This block outlines the principles and protocols related to: sample preparation/pretreatment; analytical technique; instrumental measurement methods; reporting units and performance criteria as defined by the method detection limit (MDL).
As with the sampling block, this information is presented with recommended, alternate or, in some cases, not recommended approaches for the analysis of wastewater samples.

QUALITY CONTROL SAMPLES

This block outlines the requirements for laboratory and field QC samples.

Laboratory QC samples include: blanks, spiked blanks, spiked samples and replicates and each is identified as to need and frequency for a given ATG.

Field QC samples include: travelling blanks; travelling spiked blanks and duplicates. Again each is identified as to need and suggested frequency for a given ATG.

This information is also presented as a short checklist or user's aid in Schedule 3.

1.6 **Disclaimer**

Throughout this document the use or reference to trade names, companies or trademarks is provided only for example purposes and does not constitute endorsement of the products by the Ministry of Environment, Laboratory Services Branch.

2.0 GUIDELINES FOR SAMPLING, PRESERVATION AND STORAGE

2.1 Sampling Equipment

2.1.1 **Automated Equipment**

It is recommended that all automated and manual sampling devices and equipment, their containers and all tubing, valves and contact components be dedicated to a particular sampling site in order to minimize the possibility of cross contamination. As an alternate to this dedicated application it is the user's responsibility to demonstrate that the sampling equipment is clean, free from contamination and suited to the next location, sampling and analysis needs. Generally, the cleaning and preparation of relocated equipment should include hot water, phosphate free detergent washing, hot and cold water rinsing, distilled water rinsing and, finally, multiple rinses with the actual wastewater being sampled.

Wastewater samples are typically acquired by the use of automated equipment capable of either flow or time proportional subsampling of a wastewater stream. These autosamplers must be mechanically and electrically suited to the environment in which they will serve and in consideration of safety and accessibility; be physically located to facilitate routine use, maintenance and inspection by field staff and Ministry officials.

The three most important characteristics of automated sampling devices are:

1) materials composition;
2) temperature stability;
3) ability to obtain a representative sample.

1) *Materials composition*

All wettable surfaces that contact the wastewater sample must be inert (i.e. must not contaminate, absorb nor adsorb chemicals required to be analyzed in the wastewater sample). This requirement can generally be met through consistent use of materials such as Teflon^{R} (see also Glossary for alternate acceptable compositions), glass, stainless steel and, where dictated by sampler design and function (i.e. peristaltic type pumps), short sections of surgical grade silicone rubber tubing. This type of tubing should be preferentially replaced by Teflon^{R} or other chemically inert materials as far as possible without impairing the performance of the sampling device. Where surgical grade silicone rubber tubing is used the total length should be

kept to an absolute minimum and it is generally accepted that this should be less than 2 metres.
Particular care must be taken to ensure that this tubing and all other wettable parts are cleaned or replaced at the first indication of discolouration or fouling.

These characteristics of sampler composition can be reviewed and adapted to suit the nature and sensitivity of the chemicals to be analyzed and the testing protocols to be used. For example, if an auto sampler were applied only to the collection of samples for phosphorus analysis, then wettable surfaces could include materials of a similar composition to the containers for that test (i.e. polyethylene terephthalate or linear polyethylene as described in the tables of Section 5).

2) *Temperature Stability*

Another requirement for autosamplers is that they maintain the temperature of the sample between the freezing point of the sample and 10°C. This will require cooling and/or heating capabilities depending on location and time of year.This temperature maintenance is best monitored with a "min-max" thermometer and the readings documented in a sampler specific log book which should also incorporate repair, inspection, routine use, maintenance records, and be kept near the sampler.

3) *Ability to Obtain a Representative Sample*

Automated sampling devices can provide either: 1) a single large sample composite which can be further subdivided at the end of a predefined sampling period as suitable for the analysis to be performed or; 2) multiple individual composites which can be individually assigned to specific analytical test groups.
The latter capability can provide better flexibility and accommodate a wider range of analysis requirements by providing the option of individual container preservation - either precharged (phenolics and cyanide) or following the sampling period (metals etc.), - and multiple composite samples for specialty testing needs (i.e. oil and grease analysis requires the original container be submitted to the laboratory to be rinsed with extraction solvent).

The choice of autosampler design and capability will be dictated by site specific sampling and analysis requirements. It is, however, essential that the autosampler take its sample from a location in a wastewater/water stream that will provide a representative sample. This requirement will typically be met by sampling at a

point of thorough mixing with no excessive turbulence (loss of volatiles may occur) and at a point away from walls or surfaces of a pipe or channel that may cause insufficient mixing due to currents and eddies. The sampling location may best be determined by practical tests to account for site-specific turbulence and mixing phnomena also, the sampler must maintain the sample integrity when transferring effluent from the stream to the sample container, in particular by maintaining adequate velocities in the transport system to exceed the scour and settling velocities of the constituents of interest.
If the stream contains volatile contaminants or constituents that can evaporate or be stripped, a representative sample is best obtained at a location of uniform concentration prior to the presence of turbulence, i.e. ahead of aerated grit removal systems.

2.1.2 **Manual Equipment**

Most sampling requirements for wastewater analysis can be fulfilled by manual sampling (i.e. grab sampling) using simple field equipment including: buckets, funnels and suitable lengths of chain or dip poles. This equipment must conform to the same materials composition as the automated equipment outlined above (i.e. Teflon^{R}, stainless steel, glass, etc.). The equipment must be suited to the sampling and analysis being performed.

Generally this approach is less rugged and requires manual sampling of the wastewater stream at regular intervals over a 24 hour period, in order to obtain a representative sample. However, this manual sampling is mandatory for selected analyses such as volatile organics and sulphide (ATG 15-18 and 28A). Specific manual sampling techniques for those ATG's are presented in the following section of this manual and identified in the individual tables of Section 5.

Manual sampling can be conducted using an automated sampler in manual mode in cases of automatic mode failure.
Manual sampling can also be performed from a slip-stream and valve, after purging of the sample line, preferably into the appropriate laboratory container or into a bucket for transfer to laboratory containers.

2.2 Sample Types and Techniques

All samples obtained for analysis must be from a point in the wastewater stream that is representative of the whole stream composition. The volume of sample taken must be sufficient to allow for analysis of all required analytes plus associated quality control samples (i.e. field duplicate, laboratory replicate and spiked sample).

2.2.1 **Grab**

A grab sample is meant to represent the waste water stream at a given point in time as opposed to a composite sample which represents the wastewater stream over a longer time period (24 hours). Grab samples can be collected by using an automated sampling device in the manual mode, or by dipping an appropriate container, bucket, bottle or vial, into the wastewater stream using an appropriate retrieval device such as a chain, rope or pole. Grab samples collected for analysis of compatible ATG's may be combined in a single large container and subdivided later, or they may be collected in several individual containers, each dedicated to a specific analysis. The following types of grab samples are defined:

GRAB 1: wastewater is collected in a bucket or other container and immediately transferred to the appropriate laboratory container(s), preserved as necessary and capped.

GRAB 2: the appropriate laboratory sample container is submerged in the wastewater stream on a chain or pole until it is full; it is retrieved, preserved as necessary and capped.

GRAB 3: the wastewater is collected in a bucket as for GRAB 1 and the appropriate clean (outside as well) laboratory container (i.e. volatiles vial) is held at an angle and submerged into the liquid until it is full and air bubbles have been expelled at which time it is carefully retrieved, preserved as necessary and capped. Care must be taken to avoid sample contamination from the outside of the laboratory container or the retrieval device.

Samples for ATG 25, oil & grease, must be collected directly into the laboratory container, unless direct retrieval is impossible, to minimize unavoidable losses during transfer.

The minimum recommended sample size for a grab is 100 ml except where samples are collected directly in the 25 or 40 ml septum-capped glass vial (ATG 16-18 and 28a).

2.2.2 **Composite**

Composite samples can be collected by either automated or manual methods.

Automated composite samples can be taken either proportional to the wastewater stream flow (in which cases there must be flow sensing devices connected to the sampler) or on an equal volume/equal time basis. Both of these approaches require fully automated, programmable sampling devices.

Manual composite samples are typically taken on an equal volume/equal time basis but can be combined in proportion to flow once all subsamples have been collected. This basically represents a compositing of grab samples.

Composite samples must be collected from all process effluents. Flow proportional composites (auto 1, manual 1 for all ATG's; manual 3 for ATG 15-18 and 28a; ATG 25 samples may be collected by auto 1, manual 1 or manual 3) must be taken from variable flow process streams and from process streams for which a flow variability study was not submitted under the monitoring regulations.
In cases where the process effluent stream flow has been proven, to the director's satisfaction, to be non-variable, equal volume/equal time automated composite samplers may be used (auto 2, manual 2 for all ATG's; manual 3 for ATG 15-18 and 28a; ATG 25 samples may be collected by auto 2, manual 2 or manual 3).

Composite samples must also be collected from non-contact cooling water streams, consisting of three grab samples taken at time intervals of at least six hours over a 24-hour operating day (manual 3) or using an automated composite sampler (auto 1 or 2)

Samples from stormwater streams may be collected using automated composite samplers (auto 1 or 2) or as single grabs (grab 1, 2 or 3), as specified in the pertinent limits regulation.

Composite samples are defined as follows:

AUTO 1 Automatic equipment collecting samples proportional to wastewater stream flow at time intervals of 30 minutes or less over a 24 hour period. The number and volume of samples is to be recorded.

MANUAL 1 A minimum of 8 grab samples taken at equally spaced time intervals over a 24 hour period (i.e. every 3 hours) combined in proportion to wastewater stream flow.

AUTO 2 Automatic equipment collecting samples of equal volume at equal time intervals of 15 minutes or less over a 24 hour period. The number of samples and the volume taken is to be recorded.

MANUAL 2 A minimum of 8 grab samples taken at equally spaced time intervals over a 24 hour period (i.e. every 3 hours) combined in equal volumes.

MANUAL 3 A minimum of 3 grab samples taken at time intervals of at least 6 hours over a 24 hour period.
This technique is a specific requirement for the sampling for volatiles (ATG 16-18, 28a) and sulphide (ATG 15) and an optional approach for oil and grease/solvent extractables (ATG 25).

2.2.3 **Compositing Techniques**

Where a sample is collected in a large container and requires analysis for several groups of compounds, the wastewater must be aliquotted into the appropriate laboratory containers. Teflon® tubing and gravity suction is recommended for transfer of the wastewater to the individual laboratory. A peristaltic pump may be used to transfer the aliquots into the appropriate laboratory containers, so long as the materials in contact with the sample conform to the requirements of Section 2.1.1 - Materials Composition. The sample may also be transferred to the individual laboratory container by pouring with extreme care to avoid turbulence. These aliquoting activities must be accompanied by continuous mixing of the composite sample by using a mechanical stirrer, manual swirling or other appropriate means. A magnetic stirring bar may adsorb suspended solids containing metals, thus destroying the sample integrity.

Where grab samples are collected as part of a composite for volatiles and sulphide (ATG 15-18 and 28A), each individual sample container must be submitted to the laboratory for analysis. The

laboratory has the option of analyzing each sample and reporting the arithmetic mean or of combining equal volumes of each grab and analyzing the resulting composite.

Where grab samples are collected as part of a composite for oil and grease analysis (ATG 25), each sample container must be submitted to the laboratory as this analysis includes solvent rinsing of each container.

Another option for tests such as oil and grease (ATG 25) or sulphide (ATG 15) is to collect three equal volumes of waste water into a single pregraduated laboratory container, which has been pre-charged with perservative in the case of ATG 15.

2.2.4 **Recommended Sample Volume(s)**

Section 5 lists the minimum recommended sample volumes for each analysis. A smaller volume may be collected and submitted to a laboratory for analysis only if it is sufficient to meet all the analytical requirements including lab and field QC obligations. The volume used for analysis must also allow for the laboratory to achieve its analytical method detection limit (MDL).

2.3 Preservation

Some samples require preservation to ensure stability of the target compounds during transportation and storage or to eliminate substances which may interfere with the analysis. In some cases preservation of the sample is optional, and if selected, will allow for a longer storage period before analysis must be initiated.

Preservation requirements are outlined in section 5 for each analysis along with the relevant storage times.

Generally, samples requiring preservation must be preserved immediately upon collection, either at the end of the collection period for samples collected with an automatic sampling device or after collection of each grab sample.

Where a composite sample is collected in a large container for analysis for several ATG's, some of which require preservation, the samples must be preserved immediately following their transfer into laboratory containers.

Samples collected for cyanide (ATG 2) and phenolics (ATG 14) analysis using an automatic sampling device require separate containers and each must be pre-charged with the appropriate preservative as described in Section 5.

Where samples are to be preserved to a fixed set-point (pH, colour) care must be taken that the set point has been reached according to the best available detection technique applicable to the sampling location. This will include the use of: confined range pH paper; pocket/portable pH meters; standard colour comparison charts; etc. The use of these techniques and/or devices must not contaminate the sample.

2.4 Storage

All samples must be stored for as short a time interval as possible and under conditions that will minimize sample degradation.

Samples must be kept at temperatures above the freezing point of the waste water and under 10°C, in the dark. This means that automatic samplers must be refrigerated/heated and that samples must be transported in coolers and stored in refrigerators. Storage temperatures must be monitored, preferably with min-max thermometers, and documented in a log book.

The maximum storage times for each ATG are listed in Section 5 for each group of compounds to be analyzed.
Storage time is defined as the time interval between the end of the sample collection period (typically 24 hours for composite samples) and the initiation of analysis.

In the case of organics, where analysis is considered to be initiated by the sample extraction step, the extracts should be completely analyzed within 60 days.

Samples digested for metals analysis may be maintained in a sealed container and analyzed within 30 days.

2.5 Special Considerations and Precautions

- autosampler requirements
  - separate containers for ATG 2, 14, 25
- Sample containers for ATG 2 and 14 must be precharged with preservative;
- grab samples must be collected for ATG 15; 16-18 and 28a;
- caution on acid preservation of samples suspected of containing cyanide/sulphide and extreme ranges of pH in samples in general.

- samples of wastewaters containing strong oxidizing agents (i.e. chlorine) should be neutralized as soon as possible after sample collection to prevent oxidation/degradation of vulnerable test groups (i.e. ATG 1, 4a, 5a, 5b, 14, 16-18, M8)

3.0 *GUIDELINES FOR THE ANALYSIS OF SAMPLES*

3.1 Principles of Analysis

This section describes and provides guidance on the general principles and protocols to be followed in sample preparation, clean-up and instrumental analysis. These analytical principles and protocols are listed in Section 5 for each analytical test group (ATG).

The analysis of wastewater samples can be a very demanding and complex activity depending on the type of sample, matrix problems, the presence of co-extractive or interfering materials etc. In this regard it is necessary that laboratory analysis be performed according to tenets of good laboratory practice as well as regulatory requirements.

A few key requirements that must be met are:

- **analyses must be carried out by competent laboratory personnel in a properly equipped and maintained laboratory environment;**
- **analytical procedures must meet generally accepted principles of good laboratory practice and quality control;**
- **analytical techniques must be appropriate for the sample matrix and must lead to adequate separation and accurate identification of the compounds to be analyzed;**
- **recovery of target parameters must be optimized;**
- **analytical procedures must comply with the principles and protocols of analysis listed in Section 5.**

All wastewater samples must be analyzed according to the sample preparation and instrumental measurement principles listed for each ATG in Section 5. This includes some elements related to container materials, container pretreatment, and preservation.

Before an analytical procedure can be used for MISA purposes, the method detection limit (MDL) must be determined for each target parameter according to the protocol described in the Ministry document Estimation of Analytical Method Detection Limits (MDL), June 1991, and must be equal to or less than the values listed in Section 5 and summarized in schedule 1 for each ATG. (See Section 3.3 for details).

All analyses must be initiated within the timeframes listed as maximum storage times for each ATG in Section 5 except in unavoidable circumstances in which case analytical results must be qualified by the appropriate remark code (see Protocol for the Reporting of Analytical Data under Limits Regulations, June 1991, page 20).

Sufficient and appropriate QC samples, must be included with each set of samples being analyzed. The types and frequency of QC samples are specified in Sections 4 and 5.

3.1.1 Recommended and Alternate Techniques

Section 5 outlines recommended and alternate principles of preservation and storage times, sample preparation, and instrumental measurement.

The recommended instrumental measurement method principles must be used for characterization analyses, where the whole range of parameters are required to be analyzed.

Generally, the alternate instrumental measurement method principles are meant to be used where only a few select parameters from an ATG are required to be analyzed at a high frequency 1.e. thrice-weekly or weekly or where they represent a more cost effective approach for an on-site laboratory.

3.1.2 Container Pre-Treatment

Generally new containers do not need to be cleaned prior to use, but if they are re-used then pre-treatment or washing procedures are identified for each ATG in Section 5.

Each laboratory is responsible for ensuring that all glassware, reagents and equipment used for sampling and/or analysis are suitably clean and free from contaminants and interfering substances. The frequency and nature of cleanliness checks demonstrating acceptability of labwares is the responsibility of the laboratory.

3.1.3 Sample Preparation and Pretreatment

The task of preparation and/or pretreatment of wastewater samples prior to instrumental analysis can represent the majority of time and effort in the overall analysis scheme. Where preparation or pretreatment is required, principles and protocols to be followed are listed in Section 5. With the range of preparation/ pretreatment preparation/pretreatment techniques available, the

main consideration is to treat the sample so that it will be suitable for the instrumental technique being employed and for the matrix being analyzed.

i) Grab Samples collected for sulphide (ATG 15) and volatiles analysis (ATG 16-18 and 28a) are composited by laboratory staff to minimize losses of target parameters.

There are two options:
- each grab sample is analyzed and the mean of the three results is reported, or
- the three grabs are combined in equal volumes, by aliquoting into the suitable laboratory vessel, and a single analysis is performed.

ii) Grab samples collected for Oil and Grease (ATG 25) must also be composited in a laboratory to ensure proper solvent rinsing of each sample container.

3.1.4 **Instrumental Analysis**

Instrumental measurement methods must comply with the principles set out in Section 5 for each ATG. The recommended principles must be used for characterization whilst the alternate instrumental measurement principles may be used for routine analyses.

3.1.5 **Calibration**

All analytical instruments must be calibrated in accordance with good laboratory practice. This includes periodic multiple point calibration along with daily calibration checks using a suitable reference material to ensure that the instrumentation is functioning within specified control limits.

Calibration standards must be validated against a standard reference material, if available, as described in 4.5.

A calibration curve must be established and confirmed periodically for each analytical procedure within the range normally encountered in samples of the type being analyzed.

3.2 On-line Analyzers

On-line analyzers offer the capability to continuously monitor and report the presence and concentration of contaminants/constituents of a wastewater stream. For some types of analysis, these analyzers present an alternate approach to manual or automated sampling and laboratory analysis.

The use of on-line analyzers is approved at this time for pH (ATG 3), specific conductance (ATG 7), and DOC (ATG 5a) providing the sampling equipment and instrumentation used to satisfy the requirements are identified in the previous section regarding materials composition, temperature stability, the ability to obtain a representative sample, and that the analytical principles meet the criteria set out in section 5 for the test in question.

3.2.1 **Use, Operation and Maintenance**

On-line analyzers must be operated according to good laboratory practice principles, and maintained in good operating order. Frequency of maintenance is stream dependent. Initially, on-line analyzers must be inspected and calibrated daily to determine the time interval during which the instrument continues to operate within reasonable control limits. Subsequently the maintenance and calibration frequencies may be adjusted accordingly. These data must be documented and be available upon request.

3.2.2 **Performance Check**

At least once a month the performance of each on-line analyzer must be checked to verify its continued proper functioning. A composite sample may be collected at the location of the on-line analyzer and analyzed in a laboratory following the principles and protocols indicated in section 5 or the sample may consist of a single grab on which the measurement (1.e. pH or conductivity) is made immediately using portable, suitably calibrated field equipment. This measurement is then compared to the on-line analyzer reading at the time of sampling.

3.3 Analytical Performance Criteria

3.3.1 **Method Detection Limits (MDL)**

To ensure that all laboratories performing MISA analyses have the capability to perform these analyses at appropriate levels, they are required to determine a laboratory specific method detection limit (LMDL) for each parameter to be analyzed.

These LMDL must be determined according to the MOE protocol described in "Estimation of Analytical Method Detection Limits (MDL)", June 1991", using the sample volumes, preparation and instrumental analysis procedures which will be used for wastewater samples.
An analytical method must not be used for samples taken as part of the MISA program until all LMDL have been demonstrated to fall at or below the regulation method detection limit (RMDL) listed in Section 5.

The LMDL's are to be reported using the number of significant digits used in reporting subsequent sample data generated by that analytical method (usually 2 figures). This reporting protocol is further defined in the document entitled Protocol for the Reporting of Analytical Data June 1991.

It is recommended that LMDL determinations be repeated at least semi-annually for each parameter to be analyzed by a laboratory unless routine QC data demonstrate that no significant change has occurred in the sensitivity or the precision of the analytical procedure. The LMDL's must be re-determined whenever a method is changed.

LMDL's must be determined using the exact analytical procedures to be used for MISA samples. If samples normally contain high concentrations of target parameters and the RMDL cannot be achieved using the sample volume or dilution factor normally used, then the sample extract may be concentrated or a larger sample volume may be used to determine the LMDL. In this case any MISA sample found to contain "non-detectable" levels of target parameter at the normal dilution must be concentrated by the same factor as was used for the LMDL determination or, by a factor which allows the parameter to be detected.

If matrix interferences preclude target parameter detection near the LMDL the reporting protocol described in "Protocol for the Reporting of Analytical Data, (June 1991)" must be used.
The same applies to samples where matrix effects cause co-elution of compounds: the analytical method used for LMDL determinations and sample analyses is expected to resolve all target parameters (exceptions are listed in Schedule 1) but it is understood that there may be cases where interferences render resolution impossible. However, it is expected that the laboratory will make every reasonable effort to resolve and quantitate every required parameter. In the case where an effluent is known to contain interferences, i.e. chloride, a different detection method or additional clean-up must be used where possible.

3.4 Characterization and Open Characterization

3.4.1 **Characterization - Comprehensive Analysis**

Characterization, or sector characterization as specified in the limits regulations, includes the comprehensive analysis of all of the parameters in every ATG listed in the relevant sector regulation . These analyses must be performed using only the recommended instrumental methods listed in Section 5; alternate instrumental methods may not be used for characterizations.

3.4.2 **Organics - Open Characterization - GC/MS Scan**

Where limits regulations specify open characterization, analysis is required for both organics characterization (ATG 28a & b) and elemental scan (ATG 29).

Open characterization (ATG 28), generally known as characterization of organics, in waste water samples will give an indication of the presence of organics which might not otherwise be suspected to be present in these streams. GC/MS scan analyses must be carried out and the data interpreted according to the MOE protocol entitled "Techniques for the Gas Chromatography - Mass Spectrometry Identification of Organic Compounds in Effluents", June 1991.
GC/MS scan data must be reported according to the protocol entitled MOCHA, (MISA Organic Characterization).

The internal standards listed in section 5, for ATG 28 under the heading "Limit of Characterization" must be used as listed to facilitate comparison of data between laboratories.

3.4.3 **Inorganics - Open Characterization - Elemental Scan**

Similarly open characterization (ATG 29) or Elemental scan is the semi-quantitative analysis of waste water samples for the possible presence of 70 elements, listed in Section 5 under ATG 29.

Again, alternate instrumental methods may not be used for ATG 29 analyses.
Results for ATG 6 and 9-12 characterization analyses performed on a sample may be used for ATG 29 reporting for the corresponding open characterization.

3.5 Protocol for adoption of New Methods

A commercial or industrial laboratory wishing to use analytical procedures which venture outside of the method principles and protocols listed in Section 5 must submit their proposed modifications, new methods, or revisions to the MOE through the Joint Technical Committee (JTC) for the relevant sector(s) and the multi-sectoral Joint Analytical Working Group (JAWG).

The protocol for submission of new methods is described in the MOE publication entitled " Procedures and Criteria for Evaluating New Instrumental Measurement Method Principles (NIMMP) for the Municipal and Industrial Strtegy for Abatement (MISA) Program", October 1989.

3.6 Special Considerations and Precautions

Test Specific Precautions

The following include some of the more important precautions to be followed in the sampling and analysis of certain parameters.

Total Phosphorus Analysis (ATG 6):

The stannous chloride procedure must not be used due to linearity problems: increases in phosphorus concentration beyond a method-specific point are detected as decreases. Consequently, unexpectedly high phosphorus concentrations may not be detected.

Metals Analysis (ATG 9, 10, 12 and 29):

If the presence of cyanide or sulphide is suspected in the wastewater, care must be taken while lowering the pH to ensure adequate ventilation.

Sample container and submission sheets must contain adequate caution notes to alert laboratory staff to the presence of these chemicals.

When spiking samples care must be taken to ensure that the presence of anions will not result in the formation of insoluble compounds.

Hydrides (ATG 10)

It is recommended that plastic bottles not be precharged with concentrated nitric acid to avoid false positives for antimony.

Mercury Analysis (ATG 12)

Samples containing coloured materials; reducing agents and highly alkaline substances may require larger volume of potassium dichromate solution and nitric acid as preservatives. The amounts of preservatives to obtain coloured acidic samples should be determined and these volumes be noted on the sample bottles so that an appropriate blank compensation can be done.

Preservatives are likely to become contaminated if stored in plastic vials/bottles close to mercury and its compounds. It is recommended that preservatives be stored in glass containers and away from mercury and its salts. A periodic test for mercury should be made to ensure preservatives are uncontaminated.

Volatile Organics Analysis (ATG 16-18 and 28a)

Care must be taken to minimize losses of target parameters. The sampling point must be located upstream of turbulence in the wastewater stream. The sample should be collected directly into the laboratory container with no headspace, and the container sealed, refrigerated and analyzed as soon as possible.

Grab samples composited in the laboratory, must be handled carefully and quickly to avoid undue losses of target parameters.

Extractables, base-neutral (ATG 19)

These samples must not come into contact with any plastic or rubber material (such as disposable gloves) to avoid contamination with interfering substances such as phthalate esters.

Extractables, acid (ATG 20)

Samples must not come into contact with phenolic resins, such as Bakelite® caps, to avoid sample contamination with interfering substances.

General Organics Analyses (ATG 16-27, 28a and b)

Collection of duplicate samples is recommended for organics analyses (ATG 16-27 and 28a and b) in case problems are encountered during analysis requiring re-analysis or to fulfill QC sample requirements including use as an alternate for laboratory replicate sample or spiked sample.

Biochemical Oxygen Demand (5 day) (ATG M8)

Where the option to use an oxygen electrode is selected for BOD determination, the data must be verified by analyzing at least one sample per run by both the Winkler and oxygen electrode methods.

PCBs (ATG 27)

At present total PCB concentration calculated as an Aroclor or mixture of Aroclors is required, however, laboratories doing isomer-specific analyses may report these to LSB in addition to the MIDES report. Isomer-specific analyses may be required in the future.

Dioxins/Furans (ATG 24)

If limits are set in toxic equivalents (TEQ) the dioxins and furans must be analyzed and reported as toxic equivalents (see section 5).

4.0 QUALITY MANAGEMENT

4.1 Quality Assurance and Quality Control (QA/QC)

4.1.1 **Introduction**

All environmental analysis requires a sound quality management program. This program must include elements of quality control and assurance.

Quality Assurance is a system of activities which allows an analytical laboratory to demonstrate that it is consistently providing services of defineable quality to its clients. It is a management responsibility which ensures that appropriate Quality Control and Quality Assessment procedures are performed and documented in a dependable, timely, and economic manner.

Quality Control comprises specific activities whose purpose is to monitor and control discrete laboratory tasks so that they meet predefined criteria.

Quality Assessment comprises specific audit activities whose purpose is to review the efficacy of quality control.

Together QC and QA elements form a comprehensive Quality Management Plan (QM).

4.1.2 **Good Laboratory Practice**

There is a more fundamental level of activities in the quality management of a laboratory. These activities commonly referred to as Good Laboratory Practice (GLP) encompass elements of: good housekeeping; cleanliness, quality and consistency of supplies; availability of standard operating procedures for all routine analysis activities; application of good technique based on proper education and training; appropriate documentation of organizational and experimental purpose, tasks, procedures, observations, conclusions or results.

GLP is the ideal toward which all laboratories strive to ensure that their operations will be considered acceptable in the scientific community.

The establishment and maintenance of **GLP** and **QM** in a laboratory can be accomplished through the adoption of a standard code of practice such as those defined in Canadian Standards Association (CSA) standard Z201 or MOE publication Code of Practice for Environmental Laboratories, September 1989.

4.2 Documentation/Records Keeping

An essential element of QA/QC is documentation and record keeping for all facets of sample handling and analysis.

4.2.1 **Methods/Standards**

A formal written description of methods used to analyze samples is necessary. Bench procedures must be documented in sufficient detail to ensure proper uniform application and must be readily available to technical staff. When modifications are required because of sample matrix or other factors, they must be noted and appended to the appropriate analytical records. Bench procedures should include sample pretreatment/preparation, instrumental measurement methods and data reporting procedures. QC activities documented in the bench procedures should include instrument calibration/standardization, standards preparation and validation, frequency of use of reference standards and materials, as well as the sources of all standards and standard solutions. Bench procedures should be reviewed periodically to ensure their continued applicability to the matrices of interest.

4.2.2 **Analytical Control Status**

Protocols must be established to demonstrate that analytical systems are in control.

Control limits must be established and maintained for calibration and method blanks and should also be determined for replicate or duplicate precision, reference material accuracy and target parameter recovery.

Control charting is a highly recommended method to demonstrate control status. The number of analytes being monitored and charted for control will depend on the individual behaviour of each analyte in a given laboratory setting. However, it is usual practice to demonstrate control of all analytes for a period of at least 1 year after which time a few selected, representative analytes can be monitored and charted for control of an entire group. The pertinent data for the remaining parameters must be recorded and stored for future use, if necessary.

Under limits regulations, limited parameters must be demonstrated to be under control; selection of other representative analytes is at the analyst's discretion.

The use, monitoring and charting of reference materials is a secondary, external verification of performance. The frequency of analysis and types of certified or standard reference materials will vary between laboratories depending on availability, analysis capabilities, or responsibilities but should generally represent 10% of routine in-house QC efforts.

4.2.3 **Sampling Records**

Records of sampling and sampler maintenance must be kept current and accessible for review.

Records must include:

- date and time of all sampling activity including grab and toxicity samples and performance check samples for on-line analyzers, etc;
- temperature stability records;
- sample identifications i.e. wastewater stream, control point etc.;
- sample collection method (i.e. autosampler, 24 hour composite, grab etc.);
- identification of sampling staff;
- malfunctions and corrective action taken;
- maintenance log including frequency and type of maintenance performed (i.e. tubing changes, cleaning, reprogramming, programmer repairs etc.);
- calibration, cleaning, repair log for on-line analyzers
- any other relevant information;

Any sampling malfunctions/problems which may impact sample analysis must be communicated to the laboratories performing the analysis.

4.2.4 **Analytical Records**

Formal data recording and reporting practices must be established to ensure that the quality of a reported result is known and that it is traceable back to the raw information on which it is based.

Analytical results must be recorded and archived along with the information required to ensure traceability to all associated procedural, quality control and performance evaluation records. An archiving policy should be established to ensure retention of analytical and QA/QC records for a minimum of 3 years.

A spreadsheet format is recommended to enter, store and display data as tables or graphs.

4.2.5 **QC Sample Records**

Laboratories must maintain all records necessary to show that the analytical systems used were in control at the time of analysis. The results of these QC and performance monitoring checks should be separately tabulated and summarized for ready retrieval, evaluation and audit. They must be retained in a secure manner for review. A protocol should be established for data correction and any corrections should be made in such a manner that the original data is legible.
QC records include results of all analyses of laboratory and field QC samples, as well as spiking concentrations both in the spiking solutions and in the spiked samples.

It is recommended that a protocol be established for the frequency and content of a statistical summary of QC sample data to facilitate data review by the analyst and clients. This summary should include all QC sample types and present a statistical review for each individual test such as number of samples, range of values observed, average or mean, standard deviation, plus any other relevant mathematical or statistical summary. A spreadsheet format is recommended for this documentation. (See Figure 1).

4.3 Laboratory QC samples

Where the limits regulations refer to "analytical obligations" these include laboratory QC as described below.

4.3.1 **Types and Frequency**

Four types of laboratory QC samples must be collected and/or prepared and analyzed with each analytical run, except for a few special cases such as pH where only one QC sample need be analyzed. Section 5 lists the QC samples required for each ATG.

A set of laboratory QC samples comprises the following:
- a method blank sample which is an uncontaminated sample of water which is free of the target parameters and of any substance which may interfere with that analysis;

- a replicate sample which is an additional or second aliquot of a randomly selected sample in the analytical run. If there is insufficient sample volume for replicate analyses for ATG 19-27, a duplicate sample must be collected and analyzed.

For ATG 16-18 duplicate samples must be collected and analyzed unless the sample injection system used allows for replicate analyses of the original sample.

A replicate or duplicate sample from each effluent stream for each plant must be analyzed at least once per year: a laboratory may need to select the "random" sample replicate/duplicate for each run on a rotational basis to ensure that all effluent streams are represented by at least one set of replicate/duplicates per year.

Whether a replicate or duplicate sample is analyzed results must be correctly recorded and reported with the proper sample type code (see MIDES data users' instruction manual as a guide).

- a spiked blank sample which is a method blank sample to which known (and recorded) quantities of each target parameter have been added; the concentrations added should be 2 - 5 times the individual RMDL's.

- a spiked sample which is a randomly selected sample in the analytical run, to which known (and recorded) quantities of each target parameter have been added. Where there is insufficient sample volume, a duplicate sample must be collected, spiked and analyzed in lieu of a replicate. (See Schedule 4 for recommended spiking materials).
A sample spiked for each target parameter must be analyzed, at least once per year, for each effluent stream being analyzed (see replicate sample, above).
Whether a duplicate or a replicate sample was analyzed must be correctly recorded and reported.
Each of these QC samples must be processed through each step of the analytical procedure. The number of QC samples which must be analyzed depends on the number of samples in the analytical run.

An analytical run means a group of samples which are processed together through each step of an analytical procedure.

Where a run consists of 13 samples or fewer, a single set of four QC samples needs be analyzed at the beginning of the run. Where a run contains 14 to 27 samples, two sets of QC samples must be run, at the beginning of the run and after 14 samples. If there are 28 or more samples in a run, a minimum of three sets of QC samples must be run, at the beginning, middle and end of the run.

Where samples are analyzed for pH (ATG 3) the only QC sample required is a replicate. Where samples are analyzed for specific conductance, suspended solids, hexavalent chromium and oil and grease (ATG 5, 7, 8, and 25), the only QC samples required to be analyzed are the replicate and method blank samples.

For open characterization analyses (ATG 28a, 28b and 29), the only QC sample required to be analyzed is a method blank.

4.3.2 **Data Application**

Laboratory QC sample analysis will serve to monitor the performance of the methods, the instrumentation and the analyst.

All QC activities must be documented and detailed records must be retained for review.

QC sample results are generally expected to fall within established control limits. If this were not the case, the impact and data
quality of associated samples should be reported using appropriate remark codes or in a covering letter.

Replicate sample analysis will provide an indication of within-run precision.

Analysis of spiked blank samples will provide an indication of the efficiency of the method to recover and accurately quantify target parameters.

Results of spiked sample analysis will indicate the presence of matrix-specific interferences which may hinder accurate target parameter recovery and quantification.

Results for all QC samples must be closely monitored and reviewed periodically by responsible staff to ensure that out-of-control situations are identified and corrected.
The protocols for definition and reaction to such situations must be documented and available to laboratory staff.

Method blank sample results will establish a baseline response and indicate the presence of contamination in glassware and equipment, and cross contamination from samples containing high concentrations of target parameters or interfering substances.

Should method blank sample results fall outside the established control limits, these results must be reviewed and validated or the samples in that particular run must be re-analyzed accompanied by method blank samples, which fall within the established control limits.

If sample volume is insufficient for re-analysis, a new set of samples must be collected and analyzed, accompanied by a controlled method blank sample. This does not apply to samples which are required to be collected and analyzed daily.

Analytical results must be corrected to take into account any positive results of associated method blank sample analysis. A method blank result above the LMDL is normally considered to be a positive result.

4.4 Field QC Samples

Field QC samples indicate sampling variability and the presence of contamination.

4.4.1 **Types and Frequency**

- a duplicate sample is one of 2 separate samples collected at the same time in a manner that minimizes differences. When an autosampler is used, samples contained in separate bottles may be considered to be duplicates, otherwise duplicate samples must be collected using two automatic samplers installed at the same sampling location.
Samples collected by manual grab methods must be taken simultaneously or sequentially.
The duplicate sample must be correctly reported so as to facilitate data evaluation.
Duplicate samples should be analyzed whenever a monthly performance check sample for an on-line analyzer is transported to a laboratory for analysis.

- a travelling blank is a sample of uncontaminated water free of the analytes of interest that is prepared by the laboratory performing the analysis, brought to the sampling site, opened at least as long as the manual sampling interval or while sampler bottles are being changed and preserved as necessary, then returned to the lab for analysis.
A travelling blank is not required where an on-line analyzer is used unless the monthly performance check sample is transported to a laboratory for analysis, then a travelling blank sample should be prepared and analyzed quarterly.

The criteria or control limits for blank corrections must be determined by the laboratories on the basis of historical data and these must be documented.
Data are not normally corrected for method recovery (i.e. surrogates).

- a travelling spiked blank is a sample of uncontaminated water free of any interfering substances to which a known amount of standard solution and appropriate preservative have been added by the laboratory performing the analysis. The travelling spiked blank must be prepared within *24 hours* of accompanying the containers required for sampling at the site. The travelling spiked blank is brought to the field and returned, unopened, to the same laboratory for analysis.
(See Schedule 4 for a list of recommended spiking materials).

The travelling spiked blank must be spiked with solutions containing all the target parameters required to be analyzed. Travelling spiked blank for ATG 26 need be spiked only with dehydroabietic acid since the other parameters tend to be unstable.

It is recommended that a set of the above field QC samples be collected/prepared and analyzed once a month for parameters which are monitored daily, once a quarter for weekly parameters semi-annually for quarterly parameters, and annually for semi-annual parameters.

For characterization analyses, it is recommended that duplicate samples be collected and analyzed.

Duplicate samples should be collected for all ATG's, travelling blank samples should be prepared and analyzed for all ATG's except ATG 3 and 7 (pH and conductivity), at the frequencies listed above.

Field QC samples are not required where on-line analyzers are used unless the monthly performance checks are analyzed in a laboratory as opposed to an instantaneous field measurement, in which case it is recommended that the appropriate field QC samples be analyzed once each quarter.

Travelling spiked blanks should be prepared and analyzed for organics analyses, ATG 16 - 23, 26 and 27.

When reporting field QC results, the proper sample type codes must be used to correctly identify the samples for data evaluation.

4.4.2 **Data Application**

Each of the field QC samples provides different information about the quality of the effluent samples collected and indicates possible field contamination.

A duplicate sample provides a measure of the reproducibility of the sampling, handling and analytical techniques used.

A travelling blank sample will provide an indication of any problems with sample contamination due to extraneous volatile fractions of contaminants in the atmosphere and any contaminants introduced by handling of the sample containers.

A travelling spiked blank sample should provide an indication of the degree of degradation of the target parameters from the time of sampling to analysis.

Field QC data is an integral part of the database. All records associated with the field QC analysis, as well as the associated laboratory QC samples must be accessible for review.

4.5 Standard and Certified Reference Materials

Calibration standards must be validated against standard reference materials (SRM) if available. SRMs are used as an independent check of a system calibration. Frequency of SRM analysis will depend on the nature and historical data for the analytical system of interest. Well established, traditional, stable methods/standards may require use of SRMs on less frequent basis, while experimental, or highly variable or perishable methods/standards may need more frequent SRM analysis.

SRMs are materials that have been certified by National Research Council of Canada, the United States Environmental Protection Agency, the National Institute of Standards and Technology, or international standards organizations. If an SRM is unavailable for a particular parameter, an additional external source of calibration material should be used for validation. Prepared standards are available whose concentrations have been verified by quality management protocols.

Results of SRMs and the associated QC samples should be documented and summarized. Control limits for SRMs may be established and performance reports prepared indicating the accuracy of SRM analysis.

Certified reference materials (CRM) are samples that can be used to assess laboratory accuracy (and precision depending on method of usage). CRMs are typically matrix samples for which certain contaminants or analytes are given certified values or ranges of concentration based on multiple laboratory and method comparisons. While there are few, if any, CRMs available for wastewater analysis, a range of matrix spikes for some conventional and inorganics tests are available as an additional check on analytical performance.

5.0 Guidelines for Individual MISA Analytical Test Groups (ATG)

Laboratory Name: _____ Lab Code: _____

Contact Person: _____

Phone: _____ Date: _____

FAX: _____

MISA Client List: 1)
(Industry/Plant data 2)
affected by this data) 3)
4)
5)
6)

QC Sample Type: _____ Date Range: _____ to _____

Number of Effluent
Samples Analysed
During this time: _____

Test/Parameter		No. of QC Samples Analysed	Spike Conc.		Results Units: Results/RMDL				Recovery % (Spikes Only)			
ATG	Name		Design	Design/ RMDL	Min.	Max.	Avg.	Std. Dev.	Min.	Max.	Avg.	Std.

Figure 1

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
1	Chemical Oxygen Demand	Chemical oxygen demand (COD)	N/A *	10	mg/L
2	Total cyanide	Total cyanide	57-12-5	0.005	mg/L
3	Hydrogen ion (pH)	Hydrogen ion (pH)	N/A *	N/A	
4a	Nitrogen	Ammonia plus Ammonium	N/A *	0.25 as Nitrogen	mg/L
		Total Kjeldahl nitrogen	N/A *	0.5 as Nitrogen	
4b	Nitrogen	Nitrate + Nitrite	N/A *	0.25 as Nitrogen	mg/L
5a	Organic carbon	Dissolved organic carbon (DOC)	N/A *	0.5 as Carbon	mg/L
5b	Organic carbon	Total organic carbon (TOC)	N/A *	5 as Carbon	mg/L
6	Total phosphorus	Total phosphorus	N/A *	0.1 as Phosphorus	mg/L
7	Specific conductance	Specific conductance	N/A *	5	µS/cm
8	Suspended solids	Total suspended solids (TSS)	N/A *	5	mg/L
		Volatile suspended solids (VSS)	N/A *	10	
9	Total metals	Aluminum	7429-90-5	0.03	mg/L
		Beryllium	7440-41-7	0.01	
		Boron	7440-42-8	0.05	
		Cadmium	7440-43-9	0.002	
		Chromium	7440-47-3	0.02	
		Cobalt	7440-48-4	0.02	
		Copper	7440-50-8	0.01	
		Lead	7439-92-1	0.03	
		Lithium	7439-93-2	0.05	
		Molybdenum	7439-98-7	0.02	
		Nickel	7440-02-0	0.02	

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
9	Total metals	Silver	7440-22-4	0.03	mg/L
		Strontium	7440-24-6	0.02	
		Thallium	7440-28-0	0.03	
		Vanadium	7440-62-2	0.03	
		Zinc	7440-66-6	0.01	
10	Hydrides	Antimony	7440-36-0	0.005	mg/L
		Arsenic	7440-38-2	0.005	
		Selenium	7782-49-2	0.005	
11	Chromium (Hexavalent)	Chromium (Hexavalent) (NOTE 1)	7440-47-3	0.01	mg/L
12	Mercury	Mercury	7439-97-6	0.0001	mg/L
13	Total alkyl lead	Tetra-alkyl lead (NOTE 2)	N/A *	0.002 as Lead	mg/L
		Tri-alkyl lead (NOTE 2)	N/A *	0.002 as Lead	
14	Phenolics (4AAP)	Phenolics (4AAP)	N/A *	0.002 as Phenol	mg/L
15	Sulphide	Sulphide	N/A *	0.02	mg/L
16	Volatiles, Halogenated	1,1,2,2-Tetrachloroethane	79-34-5	4.3	µg/L
		1,1,2-Trichloroethane	79-00-5	0.6	
		1,1-Dichloroethane	75-34-3	0.8	
		1,1-Dichloroethylene	75-35-4	2.8	
		1,2-Dichlorobenzene	95-50-1	1.4	
		1,3-Dichlorobenzene	541-73-1	1.1	
		1,4-Dichlorobenzene	106-46-7	1.7	
		Bromodichloromethane	75-27-4	0.8	
		Bromoform	75-25-2	3.7	
		Bromomethane	74-83-9	3.7	
		Carbon tetrachloride	56-23-5	1.3	
		Chloroform	67-66-3	0.7	

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
16	Volatiles, Halogenated	Cis-1,3-Dichloropropylene	10061-01-5	1.4	µg/L
		Dibromochloromethane	124-48-1	1.1	
		Ethylene dibromide	106-93-4	1.0	
		Methylene chloride	75-09-2	1.3	
		Tetrachloroethylene (Perchloroethylene)	127-18-4	1.1	
		Trans-1,3-Dichloropropylene	10061-02-6	1.4	
		Trichloroethylene	79-01-6	1.9	
		Trichlorofluoromethane	75-69-4	1.0	
		1,2-Dichloroethane (Ethylene dichloride) **	107-06-2	0.8	
		1,2-Dichloropropane **	78-87-5	0.9	
		Chlorobenzene **	108-90-7	0.7	
		Chloromethane **	74-87-3	3.7	
		Trans-1,2-Dichloroethylene **	156-60-5	1.4	
		Vinyl chloride (Chloroethylene) **	75-01-4	4.0	
17	Volatiles, Non-Halogenated	Benzene	71-43-2	0.5	µg/L
		Ethylbenzene	100-41-4	0.6	
		Styrene	100-42-5	0.5	
		Toluene	108-88-3	0.5	
		o-Xylene	95-47-6	0.5	
		m-Xylene and p-Xylene (NOTE 3)	108-38-3 & 106-42-3	1.1	
18	Volatiles, Water Soluble	Acrolein	107-02-8	4.0	µg/L
		Acrylonitrile	107-13-1	4.2	
19	Extractables, Base Neutral	Acenaphthene	83-32-9	1.3	µg/L
		5-nitro Acenaphthene	602-87-9	4.3	
		Acenaphthylene	208-96-8	1.4	
		Anthracene	120-12-7	1.2	
		Benz(a)anthracene	56-55-3	0.5	
		Benzo(a)pyrene	50-32-8	0.6	
		Benzo(b)fluoranthene	205-99-2	0.7	

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
19	Extractables, Base Neutral (continued)	Benzo(g,h,i)perylene	191-24-2	0.7	µg/L
		Benzo(k)fluoranthene	207-08-9	0.7	
		Biphenyl	92-52-4	0.6	
		Camphene	79-92-5	3.5	
		1-Chloronaphthalene	90-13-1	2.5	
		2-Chloronaphthalene	91-58-7	1.8	
		Chrysene	218-01-9	0.3	
		Dibenz(a,h)anthracene	53-70-3	1.3	
		Fluoranthene	206-44-0	0.4	
		Fluorene	86-73-7	1.7	
		Indeno(1,2,3-cd)pyrene	193-39-5	1.3	
		Indole	120-72-9	1.9	
		1-Methylnaphthalene	90-12-0	3.2	
		2-Methylnaphthalene	91-57-6	2.2	
		Naphthalene	91-20-3	1.6	
		Perylene	198-55-0	1.5	
		Phenanthrene	85-01-8	0.4	
		Pyrene	129-00-0	0.4	
		Benzylbutylphthalate	85-68-7	0.6	
		Bis(2-ethylhexyl)phthalate	117-81-7	2.2	
		Di-n-butylphthalate	84-74-2	3.8	
		Di-n-octylphthalate	117-84-0	2.0	
		4-Bromophenyl phenyl ether	101-55-3	0.3	
		4-Chlorophenyl phenyl ether	7005-72-3	0.9	
		Bis(2-chloroisopropyl)ether	108-60-1	2.2	
		Bis(2-chloroethyl)ether	111-44-4	4.4	
		Diphenylether	101-84-8	0.4	
		2,4-Dinitrotoluene	121-14-2	0.8	
		2,6-Dinitrotoluene	606-20-2	0.7	
		Bis(2-chloroethoxy)methane	111-91-1	3.5	
		Diphenylamine (NOTE 4)	122-39-4	14	
		N-Nitrosodiphenylamine (NOTE 4)	86-30-6	14	
		N-Nitrosodi-n-propylamine	621-64-7	3.1	

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
20	Extractables, Acid (Phenolics)	2,3,4,5-Tetrachlorophenol	4901-51-3	0.4	µg/L
		2,3,4,6-Tetrachlorophenol	58-90-2	2.8	
		2,3,5,6-Tetrachlorophenol	935-95-5	1.6	
		2,3,4-Trichlorophenol	15950-66-0	0.6	
		2,3,5-Trichlorophenol	933-78-8	1.3	
		2,4,5-Trichlorophenol	95-95-4	1.3	
		2,4,6-Trichlorophenol	88-06-2	1.3	
		2,4-Dimethylphenol	105-67-9	7.3	
		2,4-Dinitrophenol	51-28-5	42	
		2,4-Dichlorophenol	120-83-2	1.7	
		2,6-Dichlorophenol	87-65-0	2.0	
		4,6-Dinitro-o-cresol	534-52-1	24	
		2-Chlorophenol	95-57-8	3.7	
		4-Chloro-3-methylphenol	59-50-7	1.5	
		4-Nitrophenol	100-02-7	1.4	
		m-Cresol	108-39-4	3.4	
		o-Cresol	95-48-7	3.7	
		p-Cresol	106-44-5	3.5	
		Pentachlorophenol	87-86-5	1.3	
		Phenol	108-95-2	2.4	
23	Extractables, Neutral -Chlorinated	1,2,3,4-Tetrachlorobenzene	634-66-2	0.01	µg/L
		1,2,3,5-Tetrachlorobenzene	634-90-2	0.01	
		1,2,4,5-Tetrachlorobenzene	95-94-3	0.01	
		1,2,3-Trichlorobenzene	87-61-6	0.01	
		1,2,4-Trichlorobenzene	120-82-1	0.01	
		2,4,5-Trichlorotoluene	6639-30-1	0.01	
		Hexachlorobenzene	118-74-1	0.01	
		Hexachlorobutadiene	87-68-3	0.01	
		Hexachlorocyclopentadiene	77-47-4	0.01	
		Hexachloroethane	67-72-1	0.01	
		Octachlorostyrene	29082-74-4	0.01	
		Pentachlorobenzene	608-93-5	0.01	

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
24	Chlorinated Dibenzo-p-dioxins and Dibenzofurans	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	0.020	ng/L
		Octachlorodibenzo-p-dioxin	3268-87-9	0.030	
		Octachlorodibenzofuran	39001-02-0	0.030	
		Total heptachlorinated dibenzo-p-dioxins	37871-00-4	0.030	
		Total heptachlorinated dibenzofurans	Unavailable	0.030	
		Total hexachlorinated dibenzo-p-dioxins	34465-46-8	0.030	
		Total hexachlorinated dibenzofurans	Unavailable	0.020	
		Total pentachlorinated dibenzo-p-dioxins	36088-22-9	0.020	
		Total pentachlorinated dibenzofurans	Unavailable	0.015	
		Total tetrachlorinated dibenzo-p-dioxins	41903-57-5	0.020	
		Total tetrachlorinated dibenzofurans	Unavailable	0.015	
25	Solvent Extractables	Oil and grease	N/A *	1000	µg/L
26	Fatty and Resin Acids	Abietic Acid	514-10-3	0.005	mg/L
		Chlorodehydroabietic Acid	57055-38-6	0.005	
		Dehydroabietic Acid	1740-19-8	0.005	
		Dichlorodehydroabietic Acid	N/A *	0.005	
		Isopimaric Acid	5835-26-7	0.005	
		Levopimaric Acid	79-54-9	0.005	
		Neoabietic Acid	471-77-2	0.005	
		Oleic Acid	112-80-1	0.005	
		Pimaric Acid	127-27-5	0.005	
27	Polychlorinated Biphenyls (PCBs) (Total)	PCBs (Total)	Unavailable	0.1	µg/L
28a	Open Characterization - Volatiles		N/A *	10* against 1,3-Dichlorobutane	µg/L
28b	Open Characterization - Extractables		N/A *	10* against D10 Phenanthrene	µg/L

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
29	Open Characterization - Elemental	Aluminum	7429-90-5	50*	µg/L
		Antimony	7440-36-0	50*	
		Arsenic	7440-38-2	50*	
		Barium	7440-39-3	50*	
		Beryllium	7440-41-7	50*	
		Bismuth	7440-69-9	50*	
		Boron	7440-42-8	50*	
		Cadmium	7440-43-9	50*	
		Calcium	7440-70-2	50*	
		Cerium	7440-45-1	50*	
		Cesium	7440-46-2	50*	
		Chromium	7440-47-3	50*	
		Cobalt	7440-48-4	50*	
		Copper	7440-50-8	50*	
		Dysprosium	7429-91-6	50*	
		Erbium	7440-52-0	50*	
		Europium	7440-53-1	50*	
		Gadolinium	7440-54-2	50*	
		Gallium	7440-55-3	50*	
		Germanium	7440-56-4	50*	
		Gold	7440-57-5	50*	
		Hafnium	7440-58-6	50*	
		Holmium	7440-60-0	50*	
		Indium	7440-74-6	50*	
		Iridium	7439-88-5	50*	
		Iron	7439-89-6	50*	
		Lanthanum	7439-91-0	50*	
		Lead	7439-92-1	50*	
		Lithium	7439-93-2	50*	
		Lutetium	7439-94-3	50*	
		Magnesium	7439-95-4	50*	

* Value above which organic compounds or elements must be identified and their approximate concentration determined.

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
29	Open Characterization - Elemental (continued)	Manganese	7439-96-5	50*	µg/L
		Mercury	7439-97-6	50*	
		Molybdenum	7439-98-7	50*	
		Neodymium	7440-00-8	50*	
		Nickel	7440-02-0	50*	
		Niobium	7440-03-1	50*	
		Osmium	7440-04-2	50*	
		Palladium	7440-05-3	50*	
		Phosphorus	7723-14-0	50*	
		Platinum	7440-06-4	50*	
		Potassium	7440-09-7	50*	
		Praseodymium	7440-10-0	50*	
		Rhenium	7440-15-0	50*	
		Rhodium	7440-16-6	50*	
		Rubidium	7440-17-7	50*	
		Ruthenium	7440-18-8	50*	
		Samarium	7440-19-9	50*	
		Scandium	7440-20-2	50*	
		Selenium	7782-49-2	50*	
		Silicon	7440-21-3	50*	
		Silver	7440-22-4	50*	
		Sodium	N/A *	50*	
		Strontium	7440-24-6	50*	
		Sulfur	7704-34-9	50*	
		Tantalum	7440-25-7	50*	
		Tellurium	13494-80-9	50*	
		Terbium	7440-27-9	50*	
		Thallium	7440-28-0	50*	
		Thorium	7440-29-1	50*	
		Thulium	7440-30-4	50*	
		Tin	7440-31-5	50*	

* Value above which organic compounds or elements must be identified and their approximate concentration determined.

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
29	Open Characterization - Elemental (continued)	Titanium	7440-32-6	50*	µg/L
		Tungsten	7440-33-7	50*	
		Uranium	7440-61-1	50*	
		Vanadium	7440-62-2	50*	
		Ytterbium	7440-64-4	50*	
		Yttrium	7440-65-5	50*	
		Zinc	7440-66-6	50*	
		Zirconium	7440-67-7	50*	
M1	Chloride	Chloride	N/A *	2.0	mg/L
M2	Cyanates	Cyanates	N/A *	5.0	mg/L
M3	Thiocyanates	Thiocyanates	N/A *	5.0	mg/L
M4	Weak Acid Dissociable Cyanides	Free Cyanide	N/A *	0.005	mg/L
M5	Dissolved Solids	Dissolved Solids	N/A *	20	mg/L
M6	Sulphates	Sulphates	N/A *	5.0 as Sulphate	mg/L
M7	Total Residual Oxidants	Total Residual Oxidants	N/A *	0.1	mg/L
M8	Biochemical Oxygen Demand (5 day)	Biochemical Oxygen Demand (5 day)	N/A *	5.0	mg/L
M9	Metals	Iron	7439-89-6	0.02	mg/L
		Uranium	7440-61-1	0.02	
		Magnesium	7439-95-4	0.02	
M10	Diethanolamine	Diethanolamine	111-42-2	0.1	mg/L

* Value above which organic compounds or elements must be identified and their approximate concentration determined.

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS, PARAMETERS, ANALYTICAL METHOD DETECTION LIMITS AND LIMITS OF CHARACTERIZATION

ANALYTICAL TEST GROUP	NAME	PARAMETERS	CAS #	MDL/LOC	UNITS
M11	Fibrous Chrysotile Asbestos	Fibrous Chrysotile Asbestos	N/A *	0.04	million fibres/ litre
M12	Fluoride	Fluoride	N/A *	0.1	mg/L
M13	Adsorbable Organic Halide	Adsorbable Organic Halide	N/A *	0.05	mg/L

CAS # - Chemical Abstract Service Number
N/A * - Not Applicable
** - FID/PID may be used for these parameters
NOTE 1: Analyze for hexavalent chromium only if total chromium is greater than 1.0 milligrams per litre.
NOTE 2: Analyze for alkyl leads only if total lead is greater than 1.0 milligrams per litre.
NOTE 3: m-Xylene and p-Xylene often co-elute in the analysis. A single combined result may be reported as m-Xylene.
NOTE 4: Diphenylamine & N-Nitrosodiphenylamine often co-elute in the Gas Chromatography/Mass Spectrometry (GC/MS) analysis. A single combined result may be reported as Diphenylamine.

Schedule 2 Checklist for Sampling, Preservation and Storage

MISA ATG #	Sample Type (*) Auto 1 Manual 1	Auto 2 Manual 2	Manual 3	Preservation (Y/N)	Storage Time(1) (Days)	On-line Analyzer
1	R	A		N or Y	4 or 28	
2	R	A		Y precharge	7	
3	R	A		N	4	R
4a	R	A		N or Y	3 or 10	
4b	R	A		N	5	
5a	R	A		N or Y	3 or 10	R
5b	R	A		N or Y	3 or 10	
6	R	A		N or Y	14 or 28	
7	R	A		N	4	
8	R	A		N	7	
9	R	A		Y	30	
10	R	A		N or Y	30	
11	R	A		N	5	
12	R	A		Y	7	
13	R	A		N	4	
14	R	A		Y	4 or 10	
15			M	Y	7	
16			M	Y (precharge)	7	
17			M	Y (precharge)	7	A1
18			M	Y (precharge)	7	
19	R	A		N	30	
20	R	A		N	30	
23	R	A		N	30	
24	R	A		N	30	
25	R	R	R	N	7	
26	R	A		N	30	
27	R	A		N	30	
28a			M		7	
28b	R	A		N	30	
29	R	A		Y	30	
M1	R	A		N	28	
M2	R	A		Y	7	
M3	R	A		N	7	

*Recommended = R
Alternate instrumental measurement = A
A1 pending approval through NIMMP process
Mandatory = M

(1) Note: Where Preservation indicates Y or N the unpreserved sample (N) always has the shorter storage time requirement.

Schedule 2 Checklist for Sampling, Preservation and Storage

MISA ATG #	Sample Type (*) Auto 1 Manual 1	Auto 2 Manual 2	Manual 3	Preservation (Y/N)	Storage Time(1) (Days)	On-line Analyzer
M4	R	A		Y	30	
M5	R	A		N	7	
M6	R	A		N	28	
M7			R	N	1 hour	R
M8	R	A		N	4	
M9	R	A		Y	30	
M10	R	A		N	30	
M11	R	A		N	2	
M12	R	A		N	28	
M13	R	A		N	14	

*Recommended = R
Alternate instrumental measurement = A
A1 pending approval through NIMMP process
Mandatory = M

(1) Note: Where Preservation indicates Y or N the unpreserved sample (N) always has the shorter storage time requirement.

Schedule 3 Checklist for QC Samples

MISA ATG #	Laboratory QC Required (*)				Field QC Required (*)		
	Blank	Spiked Blank	Spiked Sample	Replicate	Travel. Blank	Travel. Spiked Blank	Duplicate
1	*	*	*	*	*		*
2	*	*	*	*	*		*
3				*			*
4a	*	*	*	*	*		*
4b	*	*	*	*	*		*
5a	*	*	*	*	*		*
5b	*	*	*	*	*		*
6	*	*	*	*	*		*
7	*			*	*		*
8	*			*			*
9	*	*	*	*	*		*
10	*	*	*	*	*		*
11	*	*	*	*	*		*
12	*	*	*	*	*		*
13	*	*	*	*	*		*
14	*	*	*	*	*		*
15	*	*	*	*	*		*
16	*	*	*	*	*	*	*
17	*	*	*	*	*	*	*
18	*	*	*	*	*	*	*
19	*	*	*	*	*	*	*
20	*	*	*	*	*	*	*
23	*	*	*	*	*	*	*
24	*						*
25	*			*	*		*
26	*	*	*	*	*	*	*
27	*	*	*	*	*	*	*
28a	*				*		
28b	*				*		
29	*				*		
M1	*	*	*	*	*		*
M2	*	*	*	*	*		*
M3	*	*	*	*	*		*

Note: Frequencies of analysis for required laboratory QC samples can be found in Section 4.

Schedule 3 Checklist for QC Samples

MISA ATG #	Laboratory QC Required (*)				Field QC Required (*)		
	Blank	Spiked Blank	Spiked Sample	Replicate	Travel. Blank	Travel. Spiked Blank	Duplicate
M4	*	*	*	*	*		*
M5	*			*	*		*
M6	*	*	*	*			*
M7	*	*	*	*	*		*
M8	*	*	*	*			*
M9	*	*	*	*	*		*
M10	*	*	*	*	*		*
M11				*	*		*
M12	*	*	*	*	*		*
M13	*	*	*	*	*	*	*

Note: Frequencies of analysis for required field QC samples can be found in section 4.
Refer to ATG Guide for specific blank remarks for ATG 24 and M7

Schedule 4 List of Spiking Materials

MISA ATG #	
1	Potassium Biphthalate
2	Potassium ferri or ferro-cyanide
3	N/A
4a	Ammonium Chloride for Ammonia/Ammonium; Glycine for TKN
4b	Potassium Nitrate/Sodium Nitrite
5a	Potassium Biphthalate
5b	Potassium Biphthalate
6	Potassium Dihydrogen Phosphate
7	Potassium Chloride
8	Kaolin
9	Soluble target parameters
10	Soluble target parameters
11	Soluble target parameters
12	Soluble target parameters
13	Soluble target parameters
14	Phenol
15	Sodium cyanide
16	Target parameters
17	Target parameters
18	Target parameters
19	Target parameters
20	Target parameters
23	Target parameters
24	^{13}C labelled representatives from each congener group
25	None required
26	Target parameters
27	At least two Aroclors such as a 1242:1260 mixture
28a	None required
28b	None required
29	None required
M1	Sodium Chloride
M2	Sodium Cyanate
M3	Sodium Thiocyanate
M4	Potassium cyanide or Sodium cyanide
M5	Potassium Chloride
M6	Sodium Sulphate
M7	
M8	Glucose/Glutamic acid
M9	Soluble target parameters
M10	Diethanolamine
M11	None required
M12	Sodium Fluoride
M13	2,4,6-trichlorophenol

ATG #1 CHEMICAL OXYGEN DEMAND (COD)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^R, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 25 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none; protect from light

Alternate: H_2SO_4 to pH between 1.5 and 2 after sampling

Alternate: N/A

Maximum Sample Storage Time: 4 days unpreserved
28 days preserved

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps.

ANALYSIS

Sample Preparation

Recommended:	Preparation for measurement system as appropriate followed by reflux
Alternate:	Oven digestion at 150°C in presence of oxidizing reagents
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Colourimetric measurement of trivalent chromium or back titration
Alternate:	N/A

Method Detection Limit

Required: 10 mg/L

Precautions/Notes: Alternate instrumental measurement method may not be used for characterization

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG #2 - TOTAL CYANIDE

SAMPLING

Type

Recommended:	Auto 1 or 2
Alternate:	Manual 1 or 2

Container

Recommended:	glass or polyethylene terephthalate
Alternate:	Teflon^R, polypropylene, high or low density polyethylene, polystyrene
Not Recommended:	Contact with metallic foil

Container Pretreatment

Recommended:	generally none for new containers
Alternate:	wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended:	500 mL
Alternate:	volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended:	NaOH (cyanide free) to raise pH to 12. For Auto 1 or 2, sampler bottles must be pre-charged with preservative
Alternate:	N/A

Maximum Sample Storage Time: 7 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps. For Auto 1 or 2, sampler bottles must be pre-charged with preservative. If high cyanide is suspected, sample containers must be labelled "HAZARDOUS".

ANALYSIS

Sample Preparation

Recommended:	Acid Distillation
Alternate:	N/A
Not Recommended:	Ultraviolet light digestion

Instrumental Measurement

Recommended:	Colourimetry
Alternate:	Specific ion electrode; or polarography via the method of standard addition in the presence of suitable electrolyte

Method Detection Limit

Required:	0.005 mg/L

Precautions/Notes: Alternate instrumental measurement methods may not be used for characterization

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: *N/A*

ATG #3 - HYDROGEN ION (pH)

SAMPLING

Type

Recommended: Auto 1 or 2; on-line analyzer

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^{R}, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 50 mL

Alternate: volume required to analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 4 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps.

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: On-line analyzer, pH electrode and pH meter

Alternate: N/A

Method Detection Limit

Required: N/A

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: N/A

Spiked Blank: N/A

Spiked Sample: N/A

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: N/A

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: pH may be analyzed from same sample bottle as ATG 7 (specific conductance) and ATG 8 (TSS or VSS).

ATG #4a - AMMONIA PLUS AMMONIUM
TOTAL KJELDAHL NITROGEN (TKN)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^R, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 100 mL Ammonia plus Ammonium and TKN

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: H_2SO_4 to pH between 1.5 and 2

Maximum Sample Storage Time: unpreserved 3 days
preserved 10 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps.

ANALYSIS

Sample Preparation

Recommended:	Preparation for measurement system as appropriate i.e. distillation (Ammonia plus Ammonium), Kjeldahl type digestion (TKN)
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Colourimetry or ion selective electrode or titration or ion chromatography
Alternate:	N/A

Method Detection Limit

Required:	0.25 mg/L as Nitrogen (Ammonia plus Ammonium) 0.5 mg/L as Nitrogen (TKN)

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG #4b - NITRATE PLUS NITRITE

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^R, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 50 mLs

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 5 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps.

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Colourimetry or Ion Chromatography

Alternate: N/A

Method Detection Limit

Required: 0.25 mg/L as Nitrogen

Precautions/Notes: Results and MDL's to be reported as the sum of nitrate plus nitrite.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG #5a - DISSOLVED ORGANIC CARBON (DOC)

SAMPLING

Type

Recommended: Auto 1 or 2; on-line analyzer

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^{R}, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 100 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none; protect from light

Alternate: H_2SO_4 to pH between 1.5 and 2

Maximum Sample Storage Time: unpreserved 3 days
preserved 10 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps.

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate, followed by filtration through glass fibre filter, or analysis of the supernatant of a settled sample. Where volatile/purgeable organic carbon may represent a major portion of the DOC (i.e. more than 25%), use preparation and measurement techniques which favour inclusion of this portion in DOC results.

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Quantitative conversion of carbon to carbon dioxide (CO_2) by one of:
i) ultraviolet/persulfate digestion
ii) combustion at >800°C with a catalyst
iii) combustion at >1100°C, catalyst optional
followed by infrared or colourimetric detection

Alternate: N/A

Method Detection Limit

Required: 0.5 mg/L as carbon

Precautions/Notes: DOC may be determined directly following filtration by using a sample free of inorganic carbon or as the difference between total carbon and inorganic carbon following filtration.
If a filter is used for dissolved organic carbon, use the same type as described for suspensed solids (ATG8) and dissolved solids (ATG M5).

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: *N/A*

ATG #5b - TOTAL ORGANIC CARBON (TOC)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 100 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none; protect from light

Alternate: H_2SO_4 to pH between 1.5 and 2

Maximum Sample Storage Time: unpreserved 3 days
preserved 10 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon® container only and Teflon® lined caps.

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate. A representative sample including particles must be introduced into the measurement system in a form (i.e. homogenized) which ensures effective processing by the measurement system. Particles may be separated from the liquid with subsequent exclusive analysis of both phases. Where volatile/purgeable organic carbon may represent a major portion of the TOC (i.e. more than 25%), use preparation and measurement techniques which favour inclusion of this portion in TOC results.

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Quantitative conversion of carbon to carbon dioxide (CO_2) by one of:
i) ultra violet/persulfate digestion
ii) combustion at ≥800°C with a catalyst
iii) combustion at ≥1100°C, catalyst optional
followed by infrared or colourimetric detection.

Confirm effective processing of samples using option i) UV/persulfate digestion, by comparing results from the analyses of samples with TOC levels and concentrations of particles close to the maximum expected for the effluent/matrix, to results from the analysis of the same samples using an appropriate combustion technique. Repeat comparison whenever higher TOC levels or particle concentrations are expected.

Alternate: N/A

Method Detection Limit

Required: 5 mg/L as Carbon

Precautions/Notes: TOC may be determined directly using a sample free of inorganic carbon or as the difference between total carbon and inorganic carbon.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE
Spiked Blank: APPLICABLE
Spiked Sample: APPLICABLE
Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE
Travelling Spiked Blank: N/A
Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: TOC is required to be analyzed on any sample where ATG 8 (TSS) results are greater than 15 mg/L.

Where daily TSS results are generally greater than 15 mg/L, TOC analysis may be required once a week, as specified in the site-specific schedule, on a day when TSS >15 mg/L.

ATG #6 - TOTAL PHOSPHORUS

SAMPLING

Type

Recommended:	Auto 1 or 2
Alternate:	Manual 1 or 2

Container

Recommended:	glass or polyethylene terephthalate
Alternate:	Teflon^{R}, polypropylene, high or low density polyethylene, polystyrene
Not Recommended:	contact with metallic foil

Container Pretreatment

Recommended:	generally none for new containers
Alternate:	wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended:	75 mL
Alternate:	volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended:	none
Alternate:	H_2SO_4 to pH between 1.5 and 2
Maximum Sample Storage Time:	unpreserved 14 days preserved 28 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps.

ANALYSIS

Sample Preparation

Recommended:	Preparation for measurement system as appropriate followed by digestion with 5:1 ratio of nitric acid to sulphuric acid or Kjeldahl equivalent mixture
Alternate:	perchloric acid digestion
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Colourimetry or ICP
Alternate:	N/A
Not Recommended:	N/A

Method Detection Limit

Required:	0.1 mg/L as phosphorus

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG #7 - SPECIFIC CONDUCTANCE

SAMPLING

Type

Recommended: Auto 1 or 2; on-line analyzer

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 75 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 4 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon® container only and Teflon® lined caps.

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: On-line analyzer; conductivity meter and cell measured at 25°C or conductivity meter with temperature compensation

Alternate: N/A

Method Detection Limit

Required: 5µS/cm

Precautions/Notes: Measurement at 25°C may be achieved by use of a jacketed cell, a water bath for samples, or the preparation of a curve comparing measured conductivity with temperature (to establish a correction factor if required) for each sample matrix

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: N/A

Spiked Sample: N/A

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG #8 - TOTAL SUSPENDED SOLIDS (TSS)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^{R}, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 500 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 7 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps.

ANALYSIS

Sample Preparation

Recommended:	Preparation for measurement system as appropriate and filtration using a glass fibre filter with particle retention ≤2 micrometers
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Drying of filter and particulates at 103°C ±3°C followed by gravimetry
Alternate:	N/A

Method Detection Limit

Required:	5 mg/L

Precautions/Notes: Use of filter paper having particle retention of less than 2 micrometers may lead to elevated results. The same filter type must be used for suspended solids, dissolved organic carbon (ATG5a) and dissolved solids (ATG M5)

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	N/A
Spiked Sample:	N/A
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: Balance accuracy should be confirmed by frequent check with standard weights.

ATG #8 - VOLATILE SUSPENDED SOLIDS (VSS)

SAMPLING

Type

Recommended:	Auto 1 or 2
Alternate:	Manual 1 or 2

Container

Recommended:	glass or polyethylene terephthalate
Alternate:	Teflon^{R}, polypropylene, high or low density polyethylene, polystyrene
Not Recommended:	contact with metallic foil

Container Pretreatment

Recommended:	generally none for new containers
Alternate:	wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended:	500 mL
Alternate:	volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended:	none
Alternate:	N/A

Maximum Sample Storage Time: 7 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps.

ANALYSIS

Sample Preparation

Recommended: Perform TSS analysis

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Ignite filter at 550°C ±50°C for 4 hr or until filter weight remains constant

Alternate: N/A

Method Detection Limit

Required: 10 mg/L

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: N/A

Spiked Sample: N/A

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG #9 - TOTAL METALS

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^R, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: soak overnight in 5% HNO_3 followed by distilled water rinse, if necessary

Alternate: use new containers

Sample Volume

Recommended: 500 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: HNO_3 (containing <1 mg/L of total metals) to pH <2

Alternate: N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps.

ANALYSIS

Sample Preparation

Recommended: Nitric evaporation
Alternate: other acid digestion as appropriate
Not Recommended: N/A

Instrumental Measurement

Recommended: Flame AA or ICP or DCP or ICP/MS
Alternate: graphite furnace AAS or polarography by method of standard addition in the presence of a suitable electrolyte

Method Detection Limit

Required: See Schedule 1

Precautions/Notes: Some sector specific additional tests may appear as additions to this group (M9). Alternate instrumental measurement method may not be used for characterization.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE
Spiked Blank: APPLICABLE
Spiked Sample: APPLICABLE
Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE
Travelling Spiked Blank: N/A
Duplicate: APPLICABLE and spiked sample

NOTES/REMARKS/TIPS: Spiked blank analysis must include the entire analytical procedure, including evaporation or digestion.

ATG # 10 HYDRIDES

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^R, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: soak overnight in 5% HNO_3 followed by distilled water rinse if necessary

Alternate: use new containers

Sample Volume

Recommended: 50 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: HNO_3 (containing <1 mg/L of total metals) to pH <2, if analyzed from the same sample bottle as ATG 9

Alternate: none

Maximum Sample Storage Time: 30 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps.

ANALYSIS

Sample Preparation

Recommended:	Acid digestion
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Hydride generation in conjunction with atomic absorption or hydride generation/ICP or ICP/MS
Alternate:	Graphite furnace AAS or polarography via the method of standard additions in the presence of a suitable electrolyte

Method Detection Limit

Required:	0.005 mg/L

Precautions/Notes: Alternate instrumental measurement method may not be used for characterization

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # 11 CHROMIUM (HEXAVELANT)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass with plastic lined cap

Alternate: Teflon^{R}, with plastic lined cap

Not Recommended: contact with metallic foil, paper or cardboard

Container Pretreatment

Recommended: soak overnight in 5% HNO_3 followed by distilled water rinse if necessary

Alternate: new container

Sample Volume

Recommended: 200 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 5 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps. Analyze for ATG 11 only if total chromium is >1 mg/L. ATG 11 storage time of 5 days is shorter than ATG 9 time of 30 days. ATG 9 analysis for chromium must be completed to allow for ATG 11 analysis within specified storage time, when required.

ANALYSIS

Sample Preparation

Recommended:	none
Alternate:	Solvent extraction
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Colourimetry or AA
Alternate:	Polarography by method of standard additions in the presence of suitable electrolyte.

Method Detection Limit

Required:	0.01 mg/L

Precautions/Notes: ATG 11 storage time of 5 days is shorter than ATG 9 time of 30 days. ATG 9 analysis for chromium must be completed to allow for ATG 11 analysis within specified storage time, when required.
Alternate instrumental measurement method may not be used for characterization.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # 12 MERCURY

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass with plastic-lined cap

Alternate: Teflon^{R} with plastic-lined cap

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: soak overnight in 5% HNO_3 followed by distilled water rinse if necessary

Alternate: use new containers

Sample Volume

Recommended: 200 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: add 1-2 mL HNO_3 per 250 mL sample followed by at least 0.5 mL $K_2Cr_2O_7$ solution to produce definite, lasting yellow colour

Alternate: add $KMnO_4$ solution until pink

Maximum Sample Storage Time: 7 days

Precautions/Notes: No sample contact with metal except carbon steel or stainless steel.

ANALYSIS

Sample Preparation

Recommended:	Oxidative acid digestion
Alternate:	none
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Cold vapour AA
Alternate:	Hydride - cold vapour AA

Method Detection Limit

Required:	0.0001 mg/L

Precautions/Notes: Alternate instrumental measurement method may not be used for characterization.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # 13 TOTAL ALKYL LEAD

TETRA-ALKYL LEAD

TRI-ALKYL LEAD(-INORGANIC LIGAND)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass, clear or amber with plastic lined cap

Alternate: Teflon^{R}

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: soak overnight in 5% HNO_3 followed by distilled water rinse if necessary

Alternate: N/A

Sample Volume

Recommended: 4 L

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 4 days at < 4° C

Precautions/Notes: Fill slowly to the top, no air space, avoid turbulence. ATG 13 storage time of 4 days is shorter than ATG 9 time of 30 days. ATG 9 analysis for total lead must be completed to allow for ATG 13 analysis within specified storage time, when required.

ANALYSIS

Sample Preparation

Recommended: Liquid/liquid extraction

Alternate: Derivatization

Not Recommended:

Instrumental Measurement

Recommended: Colourimetry, using dithizone reagent or GC/AA or GC

Alternate: N/A

Method Detection Limit

Required: .002 mg/L as lead

Precautions/Notes: ATG 13 storage time is 4 days, while total lead is 30 days. Analyze for ATG 13 only if total lead > 1mg/L. ATG 9 analysis for total lead must be completed to allow for ATG 13 analysis within specified storage time when required.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: *N/A*

ATG # 14 PHENOLICS (4AAP)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass with phenolic-free cap

Alternate: Teflon^{R} with phenolic-free cap

Not Recommended: N/A

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 250 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: H_2SO_4 to pH between 1.5 and 2

Alternate: 1 mL of 3N H_3PO_4 + 120 g/L $CuSO_4*5H_2O$ solution for each 250 mL sample

Maximum Sample Storage Time: 4 days with $CuS0_4$ solution
10 days with H_2S0_4

Precautions/Notes: For Auto 1 or 2, sampler bottles must be precharged with preservative. Remove any oxidizing agents as soon as possible after sampling, but no later than 48 hours after sampling.

ANALYSIS

Sample Preparation

Recommended:	Preparation for measurement system as appropriate followed by distillation from acidified (approximately pH 4) sample.
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Colourimetry of buffered sample
Alternate:	Colourimetry of chloroform extract

Method Detection Limit

Required:	0.002 mg/L as phenol

Precautions/Notes: Alternate instrumental measurement principles method may not be used for characterization

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: *N/A*

ATG # 15 SULPHIDE

SAMPLING

Type

Recommended: Grab 1 or 2 or 3, or Manual 3

Alternate: pumps may be used when direct retrieval from stream is impossible.

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon®, polypropylene, high or low density polyethylene, polystyrene

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 250 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: 5 mL per 250 mL sample of 2N zinc acetate followed by dropwise addition of 5% sodium carbonate to pH 10

Alternate: N/A

Maximum Sample Storage Time: 7 days

Precautions/Notes: Fill slowly to the top, no air space, avoid turbulence. All sample contact surfaces should be Teflon®, glass, metallic foil, or stainless steel only. If sampling as Manual 3, preservative should be added after each fraction is collected.

ANALYSIS

Sample Preparation

Recommended:	Dissolution of precipitate
Alternate:	Decantation if needed
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Methylene blue colourimetry or specific ion electrode or ion chromatography
Alternate:	Polarography by method of standard additions in the presence of a suitable electrolyte

Method Detection Limit

Required:	0.02 mg/L

Precautions/Notes: Three grab samples must be combined in the lab immediately prior to analysis, or the three samples may be analyzed separately and an arithmetic mean reported. Alternate instrumental measurement method may not be used for characterization.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE, may use duplicate sample

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS:

ATG # 16 VOLATILES, HALOGENATED

SAMPLING

Type

Recommended: Manual 3 collected as grab 2 or 3

Alternate: Manual 3 collected as grab 1 pumps may be used when direct retrieval from stream is impossible.

Container

Recommended: glass vial with Teflon^{R}-lined septum cap

Alternate: glass with foil-lined cap

Not Recommended: N/A

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum

Alternate: cap - no pretreatment

Sample Volume

Recommended: 25 or 40 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: samples suspected to contain residual chlorine should be precharged with 80 mg $Na_2S_2O_3$ per 1L prior to sampling and stored in the dark.

Maximum Sample Storage Time: 7 days

Precautions/Notes: Fill slowly to the top, no air space, avoid turbulence. All sample contact surfaces should be Teflon^{R}, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended: Purge and trap

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/MS, capillary column

Alternate: GC/EC or Hall (ELCD), capillary column; FID/PID for select compounds (marked with ** in schedule 1)

Method Detection Limit

Required: see Schedule 1

Precautions/Notes: Three grab samples may be combined in the lab immediately prior to analysis, or the three samples may be analyzed separately and an arithmetic mean reported. Certain compounds may be analyzed using GC/FID, PID, capillary column (see Schedule 1). Alternate instrumental measurement methods may not be used for characterization.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE, may use duplicate sample

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: APPLICABLE

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # 17 VOLATILES, NON-HALOGENATED

SAMPLING

Type

Recommended: Grab 1 or 2 or 3, or Manual 3

Alternate: pumps may be used when direct retrieval from stream is impossible.

Container

Recommended: glass vial with Teflon®-lined septum caps

Alternate: glass with foil-lined caps

Not Recommended: N/A

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum

Alternate: cap-no pretreatment

Sample Volume

Recommended: 25 or 40 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: Samples suspected to contain residual chlorine should be precharged with 80 mg $Na_2S_2O_3$ per 1L prior to sampling and stored in the dark.

Maximum Sample Storage Time: 7 days

Precautions/Notes: Fill slowly to the top, no air space, avoid turbulence. All sample contact surfaces should be Teflon®, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended: Purge and trap

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/MS, Capillary column

Alternate: GC/FID or PID, capillary column

Method Detection Limit

Required: **see Schedule 1**

Precautions/Notes: Three grab samples may be combined in the lab immediately prior to analysis, or the three samples may be analyzed separately and an arithmetic mean reported.
Certain sector-specific tests may appear as additions to this test group.
Alternate instrumental measurement methods may not be used for characterization.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE, may use duplicate sample

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: APPLICABLE

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: m-Xylene and p-Xylene often co-elute in the analysis; a single result may be reported as m-Xylene.

ATG # 18 VOLATILES, WATER SOLUBLE

SAMPLING

Type

Recommended: Grab 1 or 2 or 3, or Manual 3

Alternate: pumps may be used when direct retrieval from stream is impossible.

Container

Recommended: glass vial with Teflon^{R}-lined septum caps

Alternate: glass with foil-lined caps

Not Recommended: N/A

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum

Alternate: cap - no pretreatment

Sample Volume

Recommended: 25 or 40 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: Samples suspected to contain residual chlorine should be precharged with 80 mg $Na_2S_2O_3$ per 1L prior to sampling and stored in the dark.

Maximum Sample Storage Time: 7 days

Precautions/Notes: Fill slowly to the top, no air space, avoid turbulence. All sample contact surfaces should be Teflon^{R}, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended: Purge and trap

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/MS, Capillary column

Alternate: GC/EC or Hall (ELCD) and FID/PID, capillary column

Method Detection Limit

Required: see Schedule 1

Precautions/Notes: Three grab samples must be combined in the lab immediately prior to analysis, or the three samples may be analyzed separately and an arithmetic mean reported. Alternate instrumental measurement methods may not be used for characterization.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE, may use duplicate sample

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: APPLICABLE

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # 19 EXTRACTABLES, BASE NEUTRAL

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: amber glass with Teflon®-lined caps

Alternate: Teflon® with Teflon®-lined caps

Not Recommended: N/A

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum.

Alternate: instead of baking, 3 rinses with distilled in glass hexane and/or dichloromethane, air dry. Cap - no pretreatment

Sample Volume

Recommended: 800 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: add first aliquot of extraction solvent prior to storage

Alternate: N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: All sample contact surfaces should be Teflon®, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended: Liquid/liquid extraction

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/MS, Capillary column

Alternate: High Performance Liquid Chromatography (HPLC), Ultraviolet or Fluorescence Detection for PAH's and biphenyl

Method Detection Limit

Required: see Schedule 1

Precautions/Notes: Alternate instrumental measurement method may not be used for characterization.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE, may use duplicate sample

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: APPLICABLE

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N-Nitrosodiphenylamine breaks down to Diphenylamine in the injector. A single result is reported as Diphenylamine.

ATG # 20 EXTRACTABLES, ACID (PHENOLICS)

SAMPLING

Type

Recommended:	Auto 1 or 2
Alternate:	Manual 1 or 2

Container

Recommended:	amber glass with Teflon®-lined caps
Alternate:	Teflon® with Teflon®-lined caps
Not Recommended:	foil lined caps

Container Pretreatment

Recommended:	if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum.
Alternate:	if needed, 3 rinses with distilled in glass hexane dichloromethane, or air dry. Cap - no pretreatment.

Sample Volume

Recommended:	800 mL
Alternate:	volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended:	none
Alternate:	N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: All sample contact surfaces should be Teflon®, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended:	Liquid/liquid extraction, pH adjusted to <2 if appropriate; derivitization if appropriate; cleanup.
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	GC/MS, Capillary column
Alternate:	

Method Detection Limit

Required:	see Schedule 1

Precautions/Notes:

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE, may use duplicate sample

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	APPLICABLE
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS:

ATG # 23 EXTRACTABLES, NEUTRAL CHLORINATED

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: amber glass with Teflon®-lined caps

Alternate: Teflon® with Teflon®-lined caps

Not Recommended: N/A

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum

Alternate: if needed, 3 rinses with distilled in glass hexane and/or dichloromethane, air dry. Cap - no pretreatment

Sample Volume

Recommended: 800 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: All sample contact surfaces should be Teflon®, glass, metallic foil, or stainless steel only. Avoid contact with plastics. Foil lined caps may be used if sample pH is between 6.5 and 8.5.

ANALYSIS

Sample Preparation

Recommended: Liquid/liquid extraction, neutral pH.
Cleanup if necessary.

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/ECD, dual capillary column or GC/MS capillary column

Alternate: N/A

Method Detection Limit

Required: see Schedule 1

Precautions/Notes:

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE, may use duplicate sample

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: APPLICABLE

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS:

ATG # 24 CHLORINATED DIBENZO-P-DIOXINS and FURANS

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: amber glass with Teflon^{R}-lined caps

Alternate: clear glass with Teflon^{R}-lined caps

Not Recommended:

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum

Alternate: if needed, 3 rinses with distilled in glass methanol and/or dichloromethane, air dry. Cap - no pretreatment

Sample Volume

Recommended: 4 L

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: All sample contact surfaces should be Teflon^{R}, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended:	Liquid/liquid extraction and cleanup. Sample container must be rinsed with extraction solvent.
Alternate:	If TSS >15 mg/L: filter sample, extract solids by Soxhlet using toluene, extract filtrate normally, combine both extracts
Not Recommended:	N/A

Instrumental Measurement

Recommended:	GC high resolution MS, Capillary column; low resolution MS acceptable with effective clean-up if MDL achieved
Alternate:	other GC-MS techniques, GC-MS/MS

Method Detection Limit

Required:	see Schedule 1; at least one representative from each toxic congener group must be used for MDL determination.

Precautions/Notes: The laboratory must be able to demonstrate that all glassware and equipment is free of contamination. The method requires that all samples be spiked with ^{13}C labelled surrogates.
As a minimum the spikes must include one representative from each dioxin congener group.

Analysis must be done for the 17 2,3,7,8- substituted dioxins and furans and results reported for the individual toxic congeners as well as the toxic equivalents as 2,3,7,8-tetrachlorodioxin. See table Table 1 for the ITEF equivalency factors to be used.

EPA method 1613 may be used.

It is recommended that total congeners be reported as well to ensure comparability with the historic data base and to permit inter-sector comparisons.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE*
Spiked Blank:	N/A**
Spiked Sample:	N/A***
Replicate:	N/A

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE, for each sample required to be analyzed

NOTES/REMARKS/TIPS:

**Blank sample (method blank) need not be analyzed if ^{13}C labelled compounds are used for spiked blank analysis.*

*** A separate method blank must be analyzed if native dioxins and furans are used for spiked blank analysis.*

**** A separate spiked sample need not be analyzed because method requires that ^{13}C labelled standards representing each congener group be added to each sample prior to extraction.*

TABLE 1

Toxic Equivalent (ITEF) Factors for Dioxins and Furans

Dioxin/Furan Congener	International Toxicity Equivalent Factors (ITEF)
2,3,7,8-tetrachlorodibenzodioxin	1
1,2,3,7,8-pentachlorodibenzodioxin	0.5
1,2,3,4,7,8-hexachlorodibenzodioxin	0.1
1,2,3,7,8,9-hexachlorodibenzodioxin	0.1
1,2,3,6,7,8-hexachlorodibenzodioxin	0.1
1,2,3,4,6,7,8-heptachlorodibenzodioxin	0.01
octachlorodibenzodioxin	0.001
2,3,7,8-tetrachlorodibenzofuran	0.1
2,3,4,7,8-pentachlorodibenzofuran	0.5
1,2,3,7,8-pentachlorodibenzofuran	0.05
1,2,3,4,7,8-hexachlorodibenzofuran	0.1
1,2,3,7,8,9-hexachlorodibenzofuran	0.1
1,2,3,6,7,8-hexachlorodibenzofuran	0.1
2,3,4,6,7,8-hexachlorodibenzofuran	0.1
1,2,3,4,6,7,8-heptachlorodibenzofuran	0.01
1,2,3,4,7,8,9-heptachlorodibenzofuran	0.01
octachlorodibenzofuran	0.001

ATG # 25 SOLVENT EXTRACTABLES

SAMPLING

Type

Recommended:	Grab 1 or 2 or 3, or Manual 3
Alternate:	pumps may be used when direct retrieval from stream is impossible.

Container

Recommended:	clear glass, Teflon^{R} or foil lined cap
Alternate:	N/A
Not Recommended:	amber glass, plastic

Container Pretreatment

Recommended:	generally none for new containers
Alternate:	wash with detergent if necessary, distilled water and solvent rinses

Sample Volume

Recommended:	800 mL
Alternate:	volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended:	none
Alternate:	acidification with HCl to approximately pH 2

Maximum Sample Storage Time: 7 days

Precautions/Notes: Sample must be collected directly into the laboratory container. All sample contact surfaces should be Teflon^{R}, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended: Acidify with a mineral acid to approximately pH 2. Liquid/liquid extraction plus solvent rinsings of sample containers.

Alternate: N/A

Not Recommended: use of Freon®-type solvents is discouraged due to global environmental impact

Instrumental Measurement

Recommended: Gravimetric

Alternate: Infrared spectroscopy

Method Detection Limit

Required: 1000 µg/L

Precautions/Notes: Entire sample must be analyzed; method requires that sample container be rinsed with extraction solvent.

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: N/A

Spiked Sample: N/A

Replicate: APPLICABLE, must use duplicate sample

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: Use of IR spectroscopy is encouraged to confirm the nature of the solvent extracted materials.

ATG # 26 FATTY AND RESIN ACIDS

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: amber glass with Teflon^{R}-lined caps

Alternate: Teflon^{R} with Teflon^{R}-lined caps

Not Recommended: foil lined caps

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum.

Alternate: if needed, 3 rinses with distilled in glass hexane and/or dichloromethane, air dry. Cap - no pretreatment

Sample Volume

Recommended: 800 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 7 days

Precautions/Notes: All sample contact surfaces should be Teflon^{R}, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended: pH adjusted to 9. Liquid/liquid extraction with t-butyl ether, methylation.

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/FID, Capillary column

Alternate: N/A

Method Detection Limit

Required: see Schedule 1

Precautions/Notes: Recommended methodology is MOE "Method for Resin and Fatty Acids", November 1989. Concensus validated method.

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: APPLICABLE, (if required,) to contain dehydroabietic acid only

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS:

ATG # 27 POLYCHLORINATED BIPHENYLS (PCBs) TOTAL

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: amber glass with Teflon^{R}-lined caps

Alternate: Teflon^{R} with Teflon^{R}-lined caps

Not Recommended: N/A

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum

Alternate: if needed, 3 rinses with distilled in glass hexane and/or dichloromethane, air dry. Cap - no pretreatment

Sample Volume

Recommended: 800 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: All sample contact surfaces should be Teflon^{R}, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended: Liquid/liquid extraction

Alternate: Cleanup if necessary

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/ECD, single capillary column or GC/MS, capillary column

Alternate: N/A

Method Detection Limit

Required: 0.1 µg/L

Precautions/Notes: Report as individual Aroclors, or as mixture of Aroclors, as appropriate.

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE, may use duplicate sample

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: APPLICABLE

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS:

ATG # 28a OPEN CHARACTERIZATION-VOLATILES

SAMPLING

Type

Recommended: Grab 1 or 2 or 3, or Manual 3

Alternate: pumps may be used when direct retrieval from stream is impossible.

Container

Recommended: glass with Teflon^{R}-lined caps

Alternate: N/A

Not Recommended:

Container Pretreatment

Recommended: if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum

Alternate: Cap - no pretreatment

Sample Volume

Recommended: 100 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate:

Maximum Sample Storage Time: 7 days

Precautions/Notes: Fill slowly to the top, no air space, avoid turbulence. All sample contact surfaces should be Teflon^{R}, glass, metallic foil, or stainless steel only. Avoid contact with plastics.

ANALYSIS

Sample Preparation

Recommended: Purge and trap

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/MS, Capillary column

Alternate: N/A

Limit of Characterization

Required: 10 ug/L against 1,3-Dichlorobutane

Precautions/Notes: Three grab samples may be combined in the lab immediately prior to analysis, or the three samples may be analyzed separately and an arithmetic mean reported. Analysis must be performed according to the MOE publication "Techniques for the Gas Chromatography - Mass Spectrometry Identification of Organic Compounds in Effluents" dated July 1989.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: N/A

Spiked Sample: N/A

Replicate: N/A

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: N/A

NOTES/REMARKS/TIPS: results must be reported using MOCHA, both in electronic format and hard copy.

ATG # 28b OPEN CHARACTERIZATION-EXTRACTABLES

SAMPLING

Type

Recommended:	Auto 1 or 2
Alternate:	Manual 1 or 2

Container

Recommended:	amber glass with Teflon®-lined caps
Alternate:	Glass with Teflon®-lined caps
Not Recommended:	N/A

Container Pretreatment

Recommended:	if needed, wash bottle in hot water, detergent, water, distilled water rinse. Bake at 300°C for 8h minimum.
Alternate:	if needed, 3 rinses with distilled in glass hexane and/or dichloromethane, air dry. Cap - no pretreatment

Sample Volume

Recommended:	800 mL
Alternate:	volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended:	none
Alternate:	N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: All sample contact surfaces should be Teflon®, glass, or stainless steel only. Avoid contact with plastics and metalic foil

ANALYSIS

Sample Preparation

Recommended: Liquid/liquid extraction at pH >12 (base/neutral) followed by liquid/liquid extraction at pH<2 (acids)

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: GC/MS, Capillary column; co-injection of base/neutral and acid fractions

Alternate: N/A

Limit of Characterization

Required: 10 µg/L against D10-Phenanthrene

Precautions/Notes: Analysis must be performed according to the MOE publication "Techniques for the Gas Chromatography - Mass Spectrometry Identification of Organic Compounds in Effluents" July 1989, revised December 1990.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: N/A

Spiked Sample: N/A

Replicate: N/A

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: N/A

NOTES/REMARKS/TIPS: results must be reported using MOCHA, both in electronic format and hard copy.

ATG # 29 - ELEMENTAL CHARACTERIZATION

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or Teflon^R

Alternate: polypropylene, high or low density polyethylene, polystyrene, polyethylene terephthalate

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: soak overnight in 5% HNO_3 followed by distilled water rinse, if necessary

Sample Volume

Recommended: 500 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: HNO_3 (containing < 1 mg/L of total metals) to pH<2

Alternate: N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps.

ANALYSIS

Sample Preparation

Recommended: nitric acid evaporation or other acid digestion, as appropriate

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: AA and/or ICP or DCP or ICP/MS

Alternate: none

Limit of Characterization

Required: 50 ug/L

Precautions/Notes: Analysis to be performed in accordance with MOE publication "Guidance Document for the Elemental Characterization of Liquid Waste Samples", dated July 1989.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: N/A

Spiked Sample: N/A

Replicate: N/A

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: N/A

NOTES/REMARKS/TIPS: results must be reported using MIDES, in both electronic format and hard copy.

ATG # M1 CHLORIDE

SAMPLING

Type

Recommended:	Auto 1 or 2
Alternate:	Manual 1 or 2

Container

Recommended:	glass or polyethylene terephthalate
Alternate:	Teflon®, polypropylene, high or low density polyethylene, polystyrene
Not Recommended:	contact with metallic foil

Container Pretreatment

Recommended:	generally none for new containers
Alternate:	wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended:	50 mL
Alternate:	volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended:	none
Alternate:	N/A

Maximum Sample Storage Time: 28 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon® container only and Teflon® lined caps.

ANALYSIS

Sample Preparation

Recommended:	Preparation for measurement system as appropriate
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Ion chromatography or colourimetry or titration
Alternate:	N/A

Method Detection Limit

Required:	2 mg/L

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M2 CYANATES

SAMPLING

Type

Recommended:	Auto 1 or 2
Alternate:	Manual 1 or 2

Container

Recommended:	glass or polyethylene terephthalate
Alternate:	Teflon^{R}, polypropylene, high or low density polyethylene, polystyrene
Not Recommended:	contact with metallic foil

Container Pretreatment

Recommended:	generally none for new containers
Alternate:	wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended:	100 mL
Alternate:	volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended:	add NaOH (cyanide free) to pH 12
Alternate:	N/A

Maximum Sample Storage Time: 7 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps.

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Ion chromatography

Alternate: Colourimetry

Method Detection Limit

Required: 5 mg/L

Precautions/Notes: Special care must be taken to minimize chlorine interferences in IC analysis.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M3 THIOCYANATES

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^{R}, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent, if necessary, distilled water rinses

Sample Volume

Recommended: 100 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 7 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps.

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Ion chromatography

Alternate: Colourimetry

Method Detection Limit

Required: 2 mg/L

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M4 WEAK ACID DISSOCIABLE CYANIDES (FREE CYANIDES)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^R, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: soak overnight in 5% HNO_3 followed by distilled water rinse if necessary

Alternate:

Sample Volume

Recommended: 500 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: add NaOH to pH 12

Alternate: N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps. If high cyanide is suspected, sample containers must be labelled "HAZARDOUS".

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Colourimetry

Alternate: Ion chromatography with Electro-Chemical Detection

Method Detection Limit

Required: 0.01 mg/L

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M5 DISSOLVED SOLIDS

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon®, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 100 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 7 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon® container only and Teflon® lined caps.

ANALYSIS

Sample Preparation

Recommended: Filter through glass fibre filter (particle retention size ≤2 micrometers)

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Gravimetry after drying at 103°C 3°C

Alternate: N/A

Method Detection Limit

Required: 20 mg/L

Precautions/Notes: Use of filter paper retaining particles finer than 2 micrometers may lead to lower results. The same filter type must be used for dissolved solids suspended solids (ATG#8) and dissolved organic carbon (ATG 5a)

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: N/A

Spiked Sample: N/A

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M6 SULPHATES

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon®, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 50 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 28 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon® container only and Teflon® lined caps.

ANALYSIS

Sample Preparation

Recommended:	Preparation for measurement system as appropriate
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Ion chromatography
Alternate:	N/A

Method Detection Limit

Required:	5 mg/L as Sulphate

Precautions/Notes:

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M7 TOTAL RESIDUAL OXIDANTS

SAMPLING

Type

Recommended: on-line analyzer

Alternate: Manual 1 or 2 , with immediate analysis of each grab

Container

Recommended: glass with ground glass stopper

Alternate: N/A

Not Recommended:

Container Pretreatment

Recommended: none

Alternate:

Sample Volume

Recommended: 100 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none, protect from light

Alternate: N/A

Maximum Sample Storage Time: <1 hour

Precautions/Notes: Fill container completely, mount stopper to eliminate headspace

ANALYSIS

Sample Preparation

Recommended: N/A

Alternate: N/A

Not Recommended:

Instrumental Measurement

Recommended: Amperometry or potentiometry

Alternate: N/A

Method Detection Limit

Required: 0.1 mg/L as chlorine

Precautions/Notes: Each sample must be analyzed within the 1 hour storage time specified above.

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE, see note below

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: Travelling blank need not be analyzed if sample analysis occurs immediately after sampling at the sampling point.

ATG # M8 BIOCHEMICAL OXYGEN DEMAND (5 DAY)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^R, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 500 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none; protect from light

Alternate: N/A

Maximum Sample Storage Time: 4 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps.

ANALYSIS

Sample Preparation

Recommended: Preparation for measurement system as appropriate; i.e. destruction of chlorine, neutralization of pH, stabilization of sample to 20°C. Preparation of seed and dilution water as appropriate. Dilution of sample to provide adequate oxygen depletion during 5 day period.

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Dissolved oxygen determination by Winkler method or by oxygen electrode verified by Winkler method for one sample or standard per analytical run on days of analysis.

Alternate: N/A

Method Detection Limit

Required: 5 mg/L

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE, see note below

Spiked Sample: APPLICABLE, see note below

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: N/A

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: For each analytical run perform a BOD5 test on seeded dilution water, and a BOD5 test on the seeded dilution water spiked with one or more organic compounds; i.e. glucose and glutamic acid. It is recommended that the results of the seeded dilution water be used to correct seeded sample results and that the spiked seeded dilution water be used as a recovery check against established control limits.

ATG # M9 - IRON, URANIUM, MAGNESIUM

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^R, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with aluminum foil

Container Pretreatment

Recommended: soak overnight in 5% HNO_3 followed distilled water rinses, if necessary

Sample Volume

Recommended: 100 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: HNO_3 (containing < 1 mg/L of total metals) to pH<2

Alternate: none

Maximum Sample Storage Time: 30 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^R container only and Teflon^R lined caps.

ANALYSIS

Sample Preparation

Recommended:	nitric acid evaporation or other as appropriate
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Iron and Magnesium: AA or ICP or DCP or ICP/MS Uranium: Fluorescence Spectroscopy or ICP/MS
Alternate:	Magnesium: EDTA Titration

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M10 DIETHANOLAMINE

SAMPLING

Type

Recommended: Auto 1 or 2
Alternate: Manual 1 or 2

Container

Recommended: amber glass bottle
Alternate: N/A
Not Recommended: N/A

Container Pretreatment

Recommended: none
Alternate: N/A

Sample Volume

Recommended: 100 mL
Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none
Alternate: N/A

Maximum Sample Storage Time: 30 days

Precautions/Notes:

ANALYSIS

Sample Preparation

Recommended: none
Alternate: N/A
Not Recommended: N/A

Instrumental Measurement

Recommended: Ion Chromatography
Alternate: N/A

Method Detection Limit

Required: 0.1 mg/L

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES AND DATA USE

Laboratory QC Samples

Blank: APPLICABLE
Spiked Blank: APPLICABLE
Spiked Sample: APPLICABLE
Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE
Travelling Spiked Blank: N/A
Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M11 FIBROUS CHRYSOTILE ASBESTOS

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: plastic container, never before used

Alternate: N/A

Not Recommended: N/A

Container Pretreatment

Recommended: none, container must be new

Alternate: N/A

Sample Volume

Recommended: 1000 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 2 days before filtration, unlimited after, dependent on reporting time requirement

Precautions/Notes: Wide-mouth sample containers are preferable. Do not agitate so that clusters are broken into fibres.

ANALYSIS

Sample Preparation

Recommended:	Filtration onto membrane filter
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Transmission Electron Microscopy, with electron diffraction
Alternate:	N/A

Method Detection Limit

Required:	0.04 million fibres/L

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	N/A
Spiked Blank:	N/A
Spiked Sample:	N/A
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS:

ATG # M12 FLUORIDE

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: glass or polyethylene terephthalate

Alternate: Teflon^{R}, polypropylene, high or low density polyethylene, polystyrene

Not Recommended: contact with metallic foil

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 50 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: N/A

Maximum Sample Storage Time: 28 days

Precautions/Notes: If sample is expected to have high (>5%) hydrocarbons or organic solvents content, use glass or Teflon^{R} container only and Teflon^{R} lined caps.

ANALYSIS

Sample Preparation

Recommended:	Preparation for measurement system as appropriate
Alternate:	N/A
Not Recommended:	N/A

Instrumental Measurement

Recommended:	Colourimetry, ion selective electrode or Ion Chromatography
Alternate:	N/A

Method Detection Limit

Required:	0.1 mg/L

Precautions/Notes: N/A

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank:	APPLICABLE
Spiked Blank:	APPLICABLE
Spiked Sample:	APPLICABLE
Replicate:	APPLICABLE

Field QC Samples

Travelling Blank:	APPLICABLE
Travelling Spiked Blank:	N/A
Duplicate:	APPLICABLE

NOTES/REMARKS/TIPS: N/A

ATG # M13 ADSORBABLE ORGANIC HALIDE (AOX)

SAMPLING

Type

Recommended: Auto 1 or 2

Alternate: Manual 1 or 2

Container

Recommended: amber glass with Teflon^{R} lined cap

Alternate: Teflon^{R} with Teflon^{R} lined cap

Not Recommended: N/A

Container Pretreatment

Recommended: generally none for new containers

Alternate: wash with detergent if necessary, distilled water rinses

Sample Volume

Recommended: 1000 mL

Alternate: volume required to meet MDL's and analyze all applicable QC samples

Preservation

Recommended: none

Alternate: On arrival at laboratory, if analysis cannot be performed immediately, to 1 L of sample, add nitric acid to pH 2 then 1 mL 0.1M sodium sulphite solution

Minimum Sample Storage Time: 14 days

Precautions/Notes:

ANALYSIS

Sample Preparation

Recommended: Carbon adsorption (column or shaker) at pH 2 followed by nitrate wash, Dohrmann charcoal 100-200 mesh granular activated carbon or equivalent.

Alternate: N/A

Not Recommended: N/A

Instrumental Measurement

Recommended: Pyrolysis in an oxygen rich atmosphere followed by microcoulometric analysis

Alternate: N/A

Method Detection Limit

Required: 0.05 mg/L, based on 2,4,6-Trichlorophenol

Precautions/Notes: Analysis should be carried out in an environment free of chlorinated solvents

QUALITY CONTROL SAMPLES

Laboratory QC Samples

Blank: APPLICABLE

Spiked Blank: APPLICABLE

Spiked Sample: APPLICABLE

Replicate: APPLICABLE

Field QC Samples

Travelling Blank: APPLICABLE

Travelling Spiked Blank: APPLICABLE

Duplicate: APPLICABLE

NOTES/REMARKS/TIPS: N/A

6.0 GLOSSARY

ANALYTICAL RUN: a group of samples processed together through each step of an analytical procedure;

AA: atomic absorption;

ATG: analytical test group as listed in schedule 3 of the General Regulation and schedule 1 of this document;

AUTOSAMPLER: device to collect samples automatically either in proportion to the waste water flow or as equal volumes at equal time intervals;

Bakelite^{R}: registered trademark of Union Carbide Canada Ltd for phenol formaldehyde resin;

BLANK: same as method blanks;

CHARACTERIZATION: analysis of a sample to identify and quantify all the parameters listed in the applicable sector specific regulation;

COMPOSITE SAMPLE: volume of waste water made up of sub-samples or aliquots which have been combined automatically or manually or obtained from a slip-stream to an online analyzer;

CRM: Certified Reference Material; matrix sample containing analytes at concentration values which have been certified by multiple laboratory analysis;

CSA Canadian Standards Association;

DUPLICATE: duplicate sample or one of two samples collected at a sampling point at the same time in a manner that minimizes differences between the samples;

DCP: direct current plasma;

ECD: electron capture detector;

FID: flame ionization detector;

Freon^{R}:	chlorofluorocarbon, trademark of E.I. Du Pont De Nemours & Company;
GC:	gas chromatography;
GC/MS:	gas liquid chromatography/mass spectrometry;
GENERAL REGULATION:	Effluent Monitoring Regulation - or Ontario Regulation 695/88 as amended to Ontario Regulation 533/89;
GLP:	good laboratory practice, see section 4;
GRAB SAMPLE:	volume of effluent of at least 100 mL, collected over a period not exceeding 15 minutes and immediately transferred to an appropriate laboratory sample container(see section 5);
ICP:	inductively coupled plasma;
INSPECTION SAMPLE:	sample collected by a provincial officer from a sampling point of a discharger;
HPLC:	High Performance Liquid Chromatography;
JAWG:	multi-setor Joint Analytical Working Group set up by LSB to facilitate cross -sector discussions of analytical issues/problems; comprises representatives from each MISA Industrial sector, Environment Canada and MOE;
JTC:	Joint Technical Committee, set up for each MISA sector and comprising representatives from Industry, Environment Canada, MISA Advisory Council and MOE to develop monitoring and limits regulations;
LSB:	Laboratory Services Branch, MOE;
LMDL:	analytical method detection limit calculated by the laboratory performing the analysis;
MANUAL SAMPLE:	a number of grab samples, 8 or 3, collected then combined either in proportion to flow or in equal volumes to form a composite sample;

MDL: analytical method detection limit or minimum concentration of a parameter necessary to infer its presence in a sample with a level of confidence greater than 99 percent;

METHOD BLANK SAMPLE: sample of uncontaminated water which is free of any target parameter and of any substance which might interfere with the analysis;

MIDES: MISA Data Entry System;

MISA: Municipal and Industrial Strategy for Abatement of the MOE;

MOCHA: MISA Organic Characterization: software programme for organic open characterization (ATG 28) data reporting;

MOE: Ontario Ministry of the Environment;

NIMMP: MOE publication entitled: "New Instrumental Measurement Method Principles";

NIST: National Institute for Standards and Technology;

NRC: National Research Council of Canada;

ON-LINE ANALYZER: device directly connected to a sampling point which can sample and analyze water automatically;

OPEN CHARACTERIZATION: semi- quantitative analysis of a sample to identify the presence of any additional organic compounds (ATG 28) and of all the elements listed in ATG 29.

PARAMETER: refers to a compound listed in an ATG;

PID: photo ionization detector;

PRECHARGED: refers to the addition of preservative to an autosampler container prior to sample collection;

QA: quality assurance; (see section 4);

QC: quality control; (see section 4);

QM: quality management; (see section 4);

REPLICATE: one of two aliquots taken from a sample;

RMDL: analytical method detection limit listed in schedule 3 of the General Regulation and in this document. The RMDL is the maximum allowable value for a LMDL;

ROUTINE: refers to analyses performed frequently (i.e. daily, thrice-weekly or weekly), as opposed to characterization, open characterization or other analyses performed at less frequent time intervals;

RUN: same as analytical run: a group of samples processed together through each step of an analytical procedure;

SAMPLE STORAGE TIME: period of time between sample collection (i.e. end of twenty four hour sample collection period) and initiation of sample analysis; maximum allowable sample storage times are listed for each ATG in section 5;

SPIKED BLANK: same as spiked method blank;

SRM: standard reference material: which has been certified by the NRC, NIST, USEPA or other agency of equal reliability;

TARGET PARAMETER: compound of interest to be analyzed individually or as part of an analytical test group;

Teflon^{R}: registered trademark of E.I.Du Pont de Nemours & Company. Where Teflon^{R} is specified other chemically inert fluorocarbon resins may be used such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA) resins, chlorotrifluoroethylene (CTFE), co-polymers of ethylene with tetrafluoroethylene (ETFE) or chlorotrifluoroethylene (TCTFE);

USEPA: US Environmental Protection Agency.

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Cette publication technique
n'est disponible qu'en anglais.

PIBS 1698

DRAFT PROTOCOL FOR THE REPORTING OF ANALYTICAL DATA

Report prepared by:

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Laboratory Services Branch
Ontario Ministry of the Environment

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PIBS 1698

MISA
Protocol Document for the Reporting of
Analytical Data

Table of Contents

PROTOCOL FOR THE REPORTING OF ANALYTICAL DATA

1.0 INTRODUCTION

This section provides an overview of the intent, scope and limitations of this guidance document. Additionally, the user is given an insight of the contents which will serve as a key to the use of this manual.

1.1 **Purpose**

This document presents the requirements of the MISA General Regulation (OR 533/89) with respect to the reporting of analytical data for all analytical test groups (ATG) except those relating to organic characterization ATG 28a, 28b, which are described elsewhere (MOCHA).

1.2 **Scope**

This document addresses the reporting of analytical data including areas of: analytical precision, method detection limits (MDLs), smallest reporting increment, truncation or round-off of measurements and "less than" values. It also addresses the use of remark and method codes.

1.3 **Limitations**

This document defines the principles and protocols related to the reporting of analytical data to the Ministry. Except for a few clearly indicated situations (e.g. MDL's), it does not stipulate how that data must be developed, managed, or maintained within the company or laboratory record system. This approach leaves room for the use of data reporting computer systems and practices which best suit existing conditions.

Information on the use of MIDES is contained in the instruction manual General User's Guide, MIDES - MISA Data Entry System (July 1991) provided with the software. That document addresses the procedures and protocols required for electronic reporting of both effluent and QA/QC data. A similar guide describes the use of MOCHA for reporting organic open characterization data (see section 7.0).

1.4 **Updates/Revisions**

This document will be reviewed on an annual basis, and revised as necessary to incorporate changes that improve clarity or reflect advancement in the understanding of data use and interpretation, based on best scientific judgement and peer review.

1.5 **Format and Content**

Each topic is addressed by the use of relevent keywords, definitions, a brief background discussion, a statement of regulatory requirements and a proposed protocol. Additional notes are provided based on questions which have arisen in the past. Where alternative or optional protocols exist these will be indicated.

2.0 LABORATORY METHOD DETECTION LIMIT (LMDL)

KEYWORDS: Analytical Repeatability
Method Detection Limit (MDL)
Laboratory Method Detection Limit (LMDL)
Regulation Method Detection Limit (RMDL)
Matrix/Interference Effects

DEFINITIONS: **Analytical repeatability** is a measure of the within-batch variability of measurements in the absence of analytical biases/mistakes or unpredictable sample matrix effects.

A **method detection limit** marks the level above which one can conclude that a measured result indicates the presence of analyte in the sample, with a stated risk that this conclusion is false. For the MDL this estimate is based on the analytical repeatability (within-batch standard deviation), and the risk is less than 1%.

The **LMDL** is a laboratory specific method detection limit calculated using the procedure described in the Ontario MOE publication Estimation of Analytical Method Detection Limits (MDL), June 1991.

The **RMDL** values for analytes required under the MISA regulation identify the upper performance limit permitted for the LMDL. RMDL values are listed in the MOE publication Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater, June 1991.

REQUIRED: The LMDL must be calculated for each regulated analyte using the procedure described in the Ontario MOE publication Estimation of Analytical Method Detection Limits (MDL), June 1991.

The value of the LMDL for each regulated analyte must be recorded to 2 significant figures (e.g. 0.032) and reported to the Ministry, along with a method code for the test procedure used (see also Method Code).

The measured LMDL must not exceed the RMDL performance criteria.

Laboratories must report all results equal to or greater than their measured LMDL.

NOTES:

The statistical procedure and concepts on which the detection limit is based may NOT incorporate allowance for errors or bias in measurement due to sample [matrix effects] or otherwise. If the result for a specific sample is suspect because of sample matrix effects the analyst may use one of several remark codes to indicate this. If these effects prevent measurement of an analyte, the analyst must estimate the level at which the interference prevents analysis. (see also Reporting Low-Level Data).

The fact that the LMDL is not greater than the RMDL must be demonstrated at least once. The analyst should demonstrate reliable precision before estimating the LMDL. Anomalous values should not be included in the calculation of analytical repeatability. The LMDLs are to be reported using the number of significant digits used in reporting subsequent sample data generated by that analytical method (usually 2 figures, e.g. 0.032). It is recommended that the LMDL be recalculated approximately every 6 months and that the associated documentation be retained, unless routine QC data demonstrate that no significant change has occurred in the sensitivity or the precision of the procedure. The LMDLs must be re-determined whenever a method is changed.

The test samples must be processed individually through the entire method including any pre-treatment. The analytical method must be defined rigourously enough to ensure that replicate measurements will be more or less 'normally distributed' i.e. clustered together. If the method is modified, a new LMDL must be determined for each affected analyte.

The size of sample analysed, and associated changes in dilution/concentration factors, affect the LMDL value proportionately. Therefore the LMDL should be determined using the routine sample aliquot and dilution factor that will be applied when analysing actual samples.

LMDLs must be determined using the exact analytical procedures to be used for MISA samples. If samples normally contain high concentrations of target parameters and the RMDL cannot be achieved using the sample volume or dilution factor normally used, the sample extract may be concentrated or a larger sample volume used to determine the LMDL. In this case any MISA sample found to contain "non-detectable" levels of target parameters at the normal dilution must be concentrated by the same factor as was used for the LMDL determination or by a factor which allows the parameters to be detected.

3.0 ROUTINE DATA REPORTING - METHOD CODES

KEYWORDS: Method code

DEFINITIONS: The method code is a six character alphanumeric code (e.g. ID000A) including two characters to identify the laboratory and four characters to identify the test method. The code is defined by the laboratory using a laboratory ID code provided by the Laboratory Services Branch.

REQUIRED: The company must report to the Ministry the names of its laboratories including sub-contracted associations, contact information, and an analytical method code and its corresponding LMDL(s) for each analytical procedure that might be used for reporting MISA test data.

Laboratories are required to document and follow the test procedures selected, and to apply the specified quality assurance and quality control practices.

Any significant changes to the method which might affect the precision, accuracy, or recovery of the method must be documented by the laboratory and reported to the company and the Ministry along with new estimates of the LMDL.

PROTOCOL: The company contacts the specialist within Water Resources Branch, MISA Office, for the appropriate Ministry Sector to request the laboratory ID codes, which are assigned by LSB, for its internal and contract laboratories.

The laboratory lists each of its methods for the MISA analytical tests for which it is responsible, and assigns a unique method code for each of the variations/combinations of sample preparation, analytical procedure and measurement detection system.

The method code includes the assigned ID code plus four characters such as 001A, 023C, etc., to reflect a method number (001) and a version (A). The minimum documentation for a method used to determine one or more tests might include:

CODE	Brief Description
ID003A	(sample prep).....entire sample (analytical workup).....acid digestion (detection system).....AAS

The laboratory must maintain a complete procedural description of the method and associated control practices for review by Ministry staff on request.

A form for reporting method codes and LMDL's is included in the Ministry document Guidelines for Preparing an Initial Report.

NOTES:

Many commercial and industrial laboratories have already been assigned their ID code and have prepared their lists of methods and method codes.

Changes in the detection system often involve a change in the physical principles and therefore affect the type and severity of interferences encountered. They may also affect precision and accuracy. The method code should reflect this, for example, code ID009A = AAS whereas ID009B = ICP.

Analysts should also participate in relevant interlaboratory comparison studies, as available, and analyze suitable certified reference materials (as available), to ensure the overall validity of their data.

MIDES includes a table of LMDL's and default method codes which must be filled in by the company prior to using MIDES. If the method used is different than the default, the correct method code must be entered at time of data entry.

3.1 ROUTINE DATA REPORTING - SIGNIFICANT DIGITS

KEYWORDS: Analytical Repeatability
Laboratory Method Detection Limit (LMDL)
Significant Digits
Smallest Reporting Increment (SRI)

REQUIRED: Laboratories must report all results equal to or greater than their predetermined Laboratory Method Detection Limit (LMDL).

Results should be reported with at least two significant digits. (see notes below).

PROTOCOL: Calculate the precision (standard deviation) of the analytical method by one of the alternatives provided in the Ontario MOE publication Estimation of Analytical Method Detection Limits (MDL), June 1991.

Determine SRI value, thus:

SRI = Standard Deviation rounded down to nearest 1, 2, or 5

Thus if the first (leftmost) digit of the estimated standard deviation is

5 or greater;	SRI = 5
2, 3 or 4;	SRI = 2
1;	SRI = 1

Example:

Standard Deviation	SRI
570	500 !
293	200 !
134	100 !
0.038	0.02
0.013	0.01
0.0088	0.005

! Right hand zeros may not be significant since they are also required to indicate the position of the decimal.

Results are reported in multiples of SRI. e.g. if SRI = 0.2, results are reported in steps of 0.2, thus ..., 6.4, 6.6, 6.8, ...

Report analytical results to the nearest SRI or to retain at least two significant digits. Three significant digits are required if the first digit on the left is a '1'.

Ensure that the units of measure are correct. Add any appropriate remark codes, and correct the default method code if necessary.

NOTES:

For the purposes of the MISA regulation two significant digits are required for most data. If result = 2.234 and SRI = 0.002 only the first two digits (2.2) are required.

Results should be reported in steps not larger than the SRI, unless at least two significant digits can be retained.

In the absence of a measurable response at or above the LMDL, or for problems regarding sample matrix, see the issue of 'Reporting Low-Level or Less-Than Data'.

Estimates of standard deviation, and therefore of LMDL and SRI, are affected by the size of the sample aliquot and any additional dilution or concentration factors. Thus, if SRI =0.002 and a 100X dilution of sample is taken, then the SRI becomes 0.2

While the SRI may be determined by the above protocol the laboratory is free to choose a lower SRI. The selected SRI must not be greater than the analytical standard deviation.

4.0 LOW-LEVEL AND LESS-THAN DATA REPORTING

KEYWORDS: Regulation Method Detection Limit (RMDL)
Laboratory Method Detection Limit (LMDL)
Smallest Reporting Increment (SRI)

DEFINITIONS: The following examples explain the usage of '<' symbol in front of a reported value when reporting 'less-than', and the remark codes used to discriminate between various types of less-than and low-level data. For these examples, assume that RMDL = 25, LMDL = 7.3, SRI = 2.

Less Thans (Interference)

A result cannot be obtained because of sample matrix interference effects, etc. Report an estimate of the upper limit for the effect of interference with a < in front of the value and the remark code <:

e.g. < 150 <

Low-Level (Below RMDL but not below LMDL)

The company/laboratory is <u>required</u> to report results in this range but may qualify them as <u>low-level</u> using the remark code <T:

e.g. 12 <T

Less Thans (Measurements Censored Below LMDL)

The company/laboratory may choose NOT to report results when they are below LMDL. MISA requires the value of LMDL be reported with a < in front and remark code <DL:

e.g. < 7.3 <DL

Very Low-Level (Below LMDL but not below SRI)

The company/laboratory may choose the option to report results in this range and may qualify them

as very low-level. Report the result and remark code <DL:

e.g. 3 <DL

Less Thans (Below SRI or Below 1/10th RMDL)

The company/laboratory chooses to report results which are below LMDL and obtains either no measurable response or a result which is very low compared to the needs of the MISA program. These are considered as 'analytical zeros'. Report the value of SRI with a < in front and remark code <W:

e.g. < 2 <W

REQUIRED: A result must be reported for all regulated analytes.

All results at or above the LMDL must be reported. If the company chooses NOT to report results below LMDL, it must report the value of LMDL preceded by a < sign and accompanied by the remark code <DL. The LMDL value should usually be reported to two figures.

PROTOCOL: All results above RMDL may be accompanied by an appropriate explanatory remark code.

Results at or above LMDL but below RMDL may be accompanied by the remark code <T.

Results below LMDL need not be reported. (see required above).

Results below LMDL but at or above SRI may be reported, accompanied by the remark code <DL, without a < in front of the result.

Results below LMDL (where LMDL is below RMDL/10) or results below SRI, (where SRI is not greater than LMDL/3), may be reported as the value of RMDL/10 or SRI (as appropriate) preceded by < and accompanied by the remark code <W.

NOTES:

In the absence of a result due to misadventure, or in the absence of an estimate of the interference limit due to sample matrix effects, the analyst must provide an explanation for the lack of a result by an attached report, and/or by use of an accepted remark code.

When the analyte cannot be measured, the analyst should provide an estimate of the minimum level of analyte that might have been measurable. This estimate is preceeded by a < sign and accompanied by the remark code <.

THE REMARK CODES <, <T, <DL, AND <W HAVE PRIORITY OVER ALL OTHER REMARK CODES WHEN REPORTING VALUES THAT REQUIRE THEIR USE.

The practice to report or not to report results below LMDL should be applied consistently once the decision has been made.

The MIDES data reporting system permits the use of a 'hot-key' to automatically enter less-thans when the measured value is below LMDL. (The LMDL values must first be entered into the MIDES LMDL table.) The hot-key causes the screen to display:

result	remark
< LMDL	<DL

For example, if LMDL = 17 and the measured value was 6, the screen would automatically show:

< 17	<DL

The data entry person can overide the < LMDL with the actual measured result when choosing to report results below LMDL. The <DL remark should remain.

Thus, the screen could be changed to show:

6	<DL

If the result was below 5 (SRI), the data entry person would then have to change both the result and the remark fields:

< 5 <W

5.0 REMARK CODES FOR DATA REPORTING (GENERAL)

KEYWORDS: Remark Codes
Attached Reports
Laboratory Method Detection Limit (LMDL)

DEFINITIONS: Three-character remark codes are provided in the MIDES data reporting system as a means for qualifying reported results or to explain the absence of a result.

REQUIRED: An analytical result must be reported for all regulated analytes when the result is at or above the LMDL. When no result is available, a written explanation must be provided.

The remark code <DL is required when censoring results below the LMDL. The value of the LMDL is reported preceeded by a < sign and accompanied by the remark code <DL.

NOTES: **The use of a remark code does not preclude the acceptance and use of the reported value by the Ministry.**

Lists of the codes are included in the MIDES manual. Extended definitions are included here to facilitate a more consistent usage. The remark codes are grouped as follows:

- Less than - Low Level Data
- Missing Data - Attached Report
- Sample Matrix Effects/Interference
- Approximate/Unreliable Data
- Compliance Problems - Miscellaneous

5.1 REMARK CODES - LESS THAN - LOW-LEVEL DATA

KEYWORDS: <, <T, <DL, <W, (<WE, <TE)

DEFINITIONS:

< **Actual result less than reported**
The reported value is preceeded by a < sign. No result is available due to matrix effects or excessive dilution. The sample does not contain more than the stated amount.

<T **A measurable trace amount, interpret with caution**
Reported value = measured value.
Value is at or > LMDL but < RMDL.
It is a tentative low-level result.

Such data requires verification against other related data. Even when results exceed the LMDL other QA/QC information may indicate the presence of biases which will affect the interpretation of this data.

<DL **Reported value = or <MDL, measured amount <MDL (non-zero)**
If reported value is preceded by < sign, the reported value = LMDL, and the measured value has NOT been reported.

If reported value is NOT preceded by < sign, the reported value = measured value, but the value is below the LMDL. It is a very low-level result.

Sufficient data of this type may assist in distinguishing between analytes which are consistently absent from those which tend to be found at low levels. This is important when evaluating for the trace presence of analytes of concern, particularly when the levels are comparable to the blank. Conclusions are subject to evaluation of QA/QC blank and spike recovery data.

<W No measurable response (zero) the reported value is the smallest observable response.

The reported value is preceeded by a < sign. Either the measured result was 'analytically zero' and no response was observed, or the response is negligible for the purposes of the MISA regulation. Sufficient data of this type suggests the absence of analyte at levels above the reported value, subject to evaluation of QA/QC spike recovery data.

5.2 REMARK CODES - MISSING DATA - ATTACHED REPORT

KEYWORDS: ?, !, !IN, !NM, AR

DEFINITIONS:

? **Late data: data not yet available: see text**
All available data must be reported within the specified deadline in order to be in compliance. If some data is not yet available from the laboratory a reason must be given.

! **No data will be reported: see textual report**
Field or laboratory accidents may prevent analysis for one or more analytes. Whenever possible fresh samples must be taken to compensate. (see guidelines on sampling and analysis).

!IN **No data:insufficient volume due to inspection**
When MOE inspectors remove some or all of the routine sample, the company is not required to provide analytical data.

!NM **No data: no effluent - no sample available**
If there is no effluent flow there can be no data.

The following code may also be used when a result is being reported

AR **Attached report**
If there is need to explain data, or the lack of data, in more depth than permitted by the use of remark codes, an attached report can be useful. (i.e. this is the code to use to describe the type or nature of poly-chlorinated biphenyls found, (if any).

5.3 REMARK CODES - SAMPLE MATRIX EFFECTS/INTERFERENCE

KEYWORDS: I, IB, IC, IM, MP, <, >

DEFINITIONS: The following interference codes are used when a result IS being reported.

I **Interference suspected**
The nature of the sample, problems during sample preparation or analysis, etc. lead the analyst to question the result. Do not use this remark indiscriminately.

IB **Interference: background**
Often relates to problems setting background correction, baseline, etc., due to noise or adjacent interfering peaks.

IC **Interference: colour**
Certain colourimetric tests may yield high results on coloured samples.

IM **Interference: Sample matrix**
Often relates to interanalyte effects which affect response factors. (e.g. coelution)

MP **Multiphase sample: result may be suspect**
The presence of fine and coarse particulates and/or an oily phase, or biomaterial, wood chips, etc., may prevent the achievement of a representative sample.

< **Actual amount less than reported**
When a result is not available due to interference the analyst should estimate and report an estimate of the 'sample detection limit' (interference limit). The estimate is preceeded by < and accompanied by the remark code <.

> **Actual amount greater than reported**
The analyst suspects that the response is suppressed by severe interference effects.

5.4 REMARK CODES - APPROXIMATE/UNRELIABLE DATA

KEYWORDS: A, AIS, UCR, UNF, UQC, USD

DEFINITIONS:

A **Approximate value**
The result is less precise or less accurate than usual, i.e. the nature of the sample prevents proper representative aliquotting.

AIS **Approximate value: Insufficient sample**
Smaller than routine aliquots degrade the precision and reliability of measurements.

UCR **Data unreliable: could not confirm by reanalysis.**
When a suspicious result is obtained the analyst will often repeat the analysis if there is sufficient sample. This indicates inability to reanalyse.

UNF **Data unreliable: container not filled to top**
Tests for many organics require a completely filled container to avoid loss into the headspace. Results will tend to be low.

UQC **Data unreliable: possible lab QC problems**
Tests for some analytes require use of the entire sample. Repeat analysis is not possible to permit correction of QC problem.

USD **Data unreliable: sample decomposition noted**
Certain analytes are particularly perishable especially when the sample is known to have changed in transit to the laboratory. (see also the code OLD to indicate excessive delay before analysis.

5.5 REMARK CODES - COMPLIANCE PROBLEMS - MISCELLANEOUS

KEYWORDS: OLD, SD, SID, SIP, Txx,

DEFINITIONS:

OLD **Old: sample exceeds maximum storage time**
The regulatiion specifies a maximum storage time before analysis. Exceeding this time may not affect results, but should be noted.

SD **Sample duplicates differ in appearance**
Field duplicates are required under the regulation to monitor the variability and reliability of sampling. When the samples look different upon arrival at the laboratory, there may be problems with sampling, transportation, or sample preservation.

SID **Sample identification questionable**
The labels don't match the submission form or the sample appears to be different than expected for the specified source.

SIP **Sample improperly preserved**
The regulation specifies the type of sample preservation required. Analyses may have been performed on a differently preserved, or unpreserved sample, because of misadventure to the proper sample. The analyses should not be done unless there is reason to believe that the result will not be significantly affected.

6.0 REPORTING OF LABORATORY QC SAMPLE DATA

KEYWORDS: Laboratory QC
Bench QC, Run QC
Summaries
Blanks, spiked blanks, spiked samples, replicates

REQUIRED: Every laboratory providing results to the MISA program must prepare a summary report of their bench or run QC data. This summary must include at least the following information for each sample type (blanks, spiked blanks, spiked sample, replicate) as applicable:

- number of actual MISA effluent samples analysed
- number of QC samples (of each type) analysed
- concentration of test analyte found
  - minimum
  - maximum
  - average
- standard deviation of concentrations found
- for spiked blank and/or spiked sample results, the design value of the spike plus minimum, maximum and average recovery
- for replicate samples the standard deviation calculated from the difference between paired results.

$$S = \frac{(D^2)}{2n}$$

Individual reports must be prepared on a quarterly basis (every 3 months) with a final annual summary report every 12 months. All reports must be available for review by Ministry regional or laboratory staff.

An example of data tabulation/presentation is shown in figure 1.

DISCUSSION: The Ministry of Environment must be able to readily access bench level QC data for the purposes of database evaluation and development of appropriate response to effluent data variability.

The information will be coupled with the laboratory specific results obtained from interlaboratory studies to increase the effectiveness of the Ministries performance management activities.

7.0 MOCHA

The MOCHA (Ministry MISA Organic Characterization) data reporting system, is to be used by industry or industry's laboratories to report organic characterization data to the Ministry. This program is supplied on 5 " floppy disks and executes on IBM compatible microcomputers running MS-DOS version 3.3. The MOCHA program generates both hard-copy and computer disk output. These items, along with a transmittal sheet, are to be forwarded to the Ministry"s regional or district office in a manner analogous to that used when reporting MISA target compound data using the MIDES system.